


Classical Scientific Papers—Chemistry

Dalton Thomson
von Liebig Davy
Berzelius Brodie

Classical 

Scientific Papers—

Chemistry [FACSIMILE REPRODUCTIONS OF
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Classical Scientific Papers— Chemistry

THE BOOK. The early decades of the twentieth century were marked by rapid and brilliant progress in our understanding of the nature of atoms; the excitement of these years is reflected in the papers published a year or so back in *Classical Scientific Papers—Physics*. In contrast, during the nineteenth century progress in theories of matter was fitful, and promising lines of research all too often turned into blind alleys. A hundred years separated the publication of Dalton's atomic theory in 1807, and the conversion to atomism of the last prominent sceptic, Wilhelm Ostwald.

The papers which appear in facsimile here show some of the great scientists of the nineteenth century groping their way towards an atomic theory which would account satisfactorily for the facts of both physics and chemistry. For in this period physicists and chemists made different demands of atomic theories; demands which began to converge only at the end of the century. Physicists wanted simple atoms to explain such complex physical properties of things as their hardness, density and elasticity; whereas chemists were interested in substances they could not decompose—the chemical elements.

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Arranged and introduced by
DAVID M. KNIGHT, M.A., D.Phil.

*Department of Philosophy
University of Durham*



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Contents

	Acknowledgements	ix
	Foreword	xi
	General Introduction	xiii
	<i>Section I</i> The Atomic Theory in Chemistry	1
1	John Dalton On Chemical Synthesis <i>A New System of Chemistry</i> , Manchester, 1808	3
2	John Dalton Inquiries concerning the Signification of the word Particle (<i>Nicholson's</i>) <i>Journal of Natural Philosophy, Chemistry and the Arts</i> , 1811, vol. 28, pages 81-8	13
3	Thomas Thomson On the Daltonian Theory of Definite Proportions in Chemical Combinations <i>Annals of Philosophy</i> , 1813, vol. 2, pages 32-43	22
4	William Hyde Wollaston The Bakerian Lecture. On the elementary Particles of certain Crystals <i>Phil. Trans.</i> , 1813, vol. 2, pages 51-63	37
5	Jacob Berzelius On the Cause of Chemical Proportions <i>Annals of Philosophy</i> , 1813, vol. 2, pages 443-54; 1814, vol. 3, pages 51-2	51
6	John Dalton Remarks on the Essay of Dr. Berzelius on the Cause of Chemical Proportions <i>Annals of Philosophy</i> , 1814, vol. 3, pages, 174-80	66

7	Jacob Berzelius An Address to those Chemists who wish to examine the Laws of Chemical Proportions, and the Theory of Chem- istry in general <i>Annals of Philosophy</i> , 1815, vol. 5, pages 122-31	74
Section II Scepticism about the Value of the Theory		85
8	William Hyde Wollaston A Synoptic Scale of Chemical Equivalents <i>Phil. Trans.</i> , 1814, vol. 104, pages 1-23	87
9	Sir Humphry Davy Presidential Address on the Occasion of the Presentation of the first Royal Medal of the Royal Society to John Dalton <i>Collected Works</i> , 1839, vol. 7, pages 92-9	110
10	William Whewell The Atomic Theory <i>Philosophy of the Inductive Sciences</i> , 1840, vol. 1, pages 405-22	119
11	Justus von Liebig Cause of Definite Proportions <i>Familiar Letters on Chemistry</i> , 1851, letter 7	137
Section III The Boscovich Atom and the Theory of Matter		145
12	Sir Humphry Davy Fragment of a Dialogue <i>Collected Works</i> , 1839, vol. 9, pages 383-8	149
13	Michael Faraday A speculation touching Electric Conduction and the Nature of Matter <i>Phil. Mag.</i> , 1844, vol. 24, pages 136-44	156
14	Sir Humphry Davy On the Analogies between Undecompounded Substances <i>Elements of Chemical Philosophy</i> , 1812, vol. 1, pages 478-89	166
15	M. J. Dumas The Faraday Lecture <i>Chemical News</i> , 1869, vol. 20, pages 1-7	179

<i>Section IV</i>	<i>Kinetic Theories</i>	187
16	J. Herapath On the Physical Constitution of the Universe <i>Annals of Philosophy</i> , 1821, vol. 17, pages 274-82	190
17	O. F. Mossotti On the Forces which regulate the Internal Constitution of Bodies (<i>Taylor's</i>) <i>Scientific Memoirs</i> , 1837, vol. 1, pages 448-51	200
18	Charles Babbage On the Great Law which regulates Matter <i>Ninth Bridgewater Treatise</i> , 1837, pages 163-9	205
19	T. Graham Speculative Ideas respecting the Constitution of Matter <i>Phil. Mag.</i> , 1864, 4th series, vol. 27, pages 81-4	213
20	J. C. Maxwell Molecules <i>Nature</i> , 1873, vol. 8, pages 437-41	217
21	J. C. Maxwell Atom <i>Encyclopaedia Britannica</i> , 1875, vol. 3, pages 36-49	222
<i>Section V</i>	<i>The Atomic Debates</i>	237
22	William Odling Presidential Address <i>Reports of the British Association</i> , 1864, pages 21-4	239
23	Benjamin C. Brodie On the Mode of Representation afforded by the Chemical Calculus, as contrasted with the Atomic Theory <i>Chemical News</i> , 1867, vol. 15, pages 295-305	243
24	A. Kekule On some points of Chemical Philosophy <i>Laboratory</i> , 1867, vol. 1, pages 303-6	255
25	A. W. Williamson On the Atomic Theory <i>J. Chemical Society</i> , 1869, vol. 22, pages 328-65	260

26	Debate on Williamson's address <i>Chemical News</i> , 1869, vol. 20, pages 235-7	299
27	E. J. Mills On Statistical and Dynamic Ideas on the Atomic Theory <i>Phil. Mag.</i> , 1871, 4th series, vol. 42, pages 112-29	302
Section VI The Problems are resolved		321
28	W. Thomson Steps towards a Kinetic Theory of Matter <i>Reports of the British Association</i> , 1884, pages 613-22	323
29	W. Crookes Presidential Address <i>Reports of the British Association</i> , 1886, pages 558-76	334
30	W. Ostwald Faraday Lecture <i>J. Chemical Society</i> , 1904, vol. 85, pages 506-22	354
31	M. Jean Perrin <i>Brownian Movement and Molecular Reality</i> , trans. Soddy, 1910, pages 1-21	371

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Foreword

Following the success a few years ago of a volume of facsimile articles on the development of atomic physics during the nineteenth century, it was felt that a comparable anthology of articles relating to chemistry, specifically on theories of matter, during the same period, would be welcomed by scholars and academic libraries.

The papers reprinted here have been selected to recapture the argument over theories of matter which raged for the century following the original publication of Dalton's atomic theory. The reader, as he follows the various controversies, is put in the position of the participants, or rather of a contemporary spectator.

The introductions to the main body of the articles and to the separate sections link the various phases of the controversy.

General Introduction

There is a temptation in looking at the history of science to suppose that ideas which are now of great importance have always been so, and that those who opposed, for example, the Copernican System or the Atomic Theory must have been reprehensibly blind. This temptation to whiggery seems worth avoiding; and this can be done if we bear in mind that a scientific theory is valuable insofar as it explains known facts, leads to new experiments, helps beginners to learn the subject, and conforms to certain canons, such as Occam's Razor—the principle that hypothetical entities should not be multiplied unnecessarily. A theory which at one time provides satisfactory explanations without undue hypothesis, and is a useful guide in the laboratory and the classroom, may at another be found unsatisfactory for scientific or for philosophical reasons. In the twentieth century the atomic theory in chemistry is invaluable; but it does not follow from this that in the nineteenth century too it was unrivalled in power or economy. The papers reprinted here, spanning the nineteenth century and stretching into the twentieth, have been chosen to recapture the controversy over theories of matter which raged for the hundred years which followed the publication of Dalton's atomic theory.

In the history of science such periods of uncertainty and controversy seem to be as characteristic as the great bursts of activity in which a number of workers build on one another's results to produce steady and rapid progress. The previous volume in this series illustrated just such a brilliant epoch, the rise of atomic physics from J. J. Thomson's paper of 1897, describing his measurement of e/m for cathode rays, through to Chadwick's discovery of the neutron only thirty-five years later. The papers in this volume are rather different. Though in a sense they illustrate progress, the gradual process by which chemists came to see that it was of advantage to have a theory of matter, and that the only real candidate was the atomic theory, this progress was highly dialectical and almost incidental. By the time all chemists had come to accept the atomic theory, it was a very different theory from that of the early Daltonian atomists. Instead of billiard ball atoms of iron, hydrogen and so on, the basic entities were protons and electrons, which, in different quantities and arrangements, were held to build up all the various chemical elements, from

which in turn chemical compounds were composed. And with the progress of chemistry in the nineteenth century, and its increasingly close links with physics, the demands made of the atomic theory in 1910 were very different from those which had been made in 1810. There was much more to explain; and many of the new phenomena, such as isomerism, could readily be explained in terms of atomism, and only in a cumbrous and unsatisfactory way on any other assumptions. The final blow to the non-atomists was the explanation in atomic terms of the Brownian Motion.

It seems worth blowing the dust from this dead controversy for a number of reasons. Nothing which has engaged the talents of scientists as eminent as those here represented deserves to be completely forgotten; and in an age of historicism, when the belief prevails that the course of history is in some way necessary, it is salutary to remind ourselves that, to some of those best qualified to judge, a non-atomic chemistry seemed a strong possibility throughout the nineteenth century. Further, one can perhaps learn more about the way the minds of scientists work by studying their perplexities rather than their successes. In works of controversy and of *haute vulgarisation* the metaphysics is often explicit, whereas in more formal papers it is suppressed. And men of science through most of the nineteenth century took seriously their title of 'natural philosophers', and sought to expound their insights and beliefs about nature, and about science, both to their fellows and to a more general readership. Finally, we shall find that the philosophical issues raised, often very lucidly, by nineteenth-century authors are by no means dead. Should scientists eschew hypothetical entities, withholding belief even if it is impossible to avoid all use of them, and seek only mathematical laws connecting observables; or would such a programme lead rapidly to sterility? Does it make sense to say of a theory that it is insufficiently simple or harmonious to be really in accord with nature; or is it impossible to arrive at universally acceptable criteria of simplicity? And should workers in a given science make every effort to share the physicists' basic conceptual scheme, and thereby 'reduce' their science to physics; or should they carry on with the methods and assumptions of their own science, at any rate until it achieves a sufficient maturity to negotiate from strength? These questions were raised by positivists, by believers in the essential unity of all matter, and by adherents to the doctrine of 'chemical atoms'.

The object of this selection is to put the reader, as he follows the various controversies, in the position of the participants, or rather of a contemporary spectator. The papers are therefore reproduced exactly as they first appeared in print. The excerpts from books are all complete sections or chapters, and most of the articles from the various journals are complete; where only parts of papers have been reproduced this is recorded in the introductions to the various sections. All the papers are in English, and only contemporary translations from other languages

have been used; this means that the reader has before him no more than a nineteenth-century Englishman who did not read French or German. Scientists from the continent of Europe are therefore relatively under-represented; in particular, there is very little on molecular theory, and there is much less of Berzelius than his importance in the story of the atomic theory in chemistry would warrant. But the beliefs and attitudes of British chemists do not seem to have been very different from those of their continental colleagues; and very similar collections of papers in different tongues could in all probability be assembled.

We should avoid the implication that the atomic theory was revived by Dalton. The atomic theories of antiquity were revived in the seventeenth century, and by 1700 almost all scientists in England were atomists. A formulation of the atomic theory to which men turned in both the eighteenth and early nineteenth centuries was that of Newton, who declared in his *Opticks* that it seemed probable that God had in the Beginning created atoms so hard that they could never break or wear away, and that everything we see is composed of these particles. But until the nineteenth century the atomic theory provided only explanations in principle; it was not sufficiently detailed to be really testable as a strictly scientific theory should be, and it was not very powerful in leading to experiments.

The object of an atomic theory is to explain the various and complicated properties of things, by showing that they follow as a matter of course from the assumption of atoms having relatively much simpler properties, and capable of being arranged in various ways. The atoms of the seventeenth- and eighteenth-century 'corpuscular philosophy' were very simple indeed. They were all composed of the same stuff, namely 'matter', and differed only in shape and size. Various arrangements of these particles formed the larger units which, in their turn, composed the various substances we encounter. To a nineteenth-century scientist like Davy, it seemed that the authority of the corpuscularians supported the conclusion that the chemical elements were made up of different arrangements of very few kinds of prime matter.

The corpuscular philosophy led to no detailed predictions or explanations, and was criticised by Stahl for scratching the surface of things and leaving the kernel untouched. Lavoisier made much the same attack; theories of matter were probably metaphysical, and certainly of little value in chemistry. 'If by the term *elements*', he wrote, 'we mean to express those simple and indestructible atoms of which matter is composed, it is extremely probable we know nothing at all about them.' Chemists should apply the term 'element' to mean 'the last point which analysis is capable of reaching'; they were not entitled to affirm that such elements were really composed of genuine atoms, but should not on the other hand suppose them to be complex without experimental evidence. Whereas the corpuscularians

took the unity and simplicity of matter for granted, Lavoisier urged chemists to recognise the limits of scientific knowledge.

But at the opening of the nineteenth century the distinction between chemical and physical atoms was still in the future. In the chemical textbooks published about 1800, the corpuscular philosophy was still usually presented at some length; and it would seem fair to say that, in general, scientists took it for granted that the world was made up of atoms. Various forces between these atoms or corpuscles were described. There was the 'attraction of aggregation' which held like particles together in solids and liquids; and the 'attraction of affinity' which held unlike particles together in chemical compounds. Chemical combination took place when the attraction of affinity between the particles of the reactants exceeded their attractions of aggregation. The corpuscular theory was incapable of accounting in more than a very general way for the phenomena of chemistry; but it did no harm to believe in it, and after all it had received the approbation of Newton. Chemists carefully compared their use of 'attraction' with the Newtonian usage as a descriptive, not explanatory, term. They hoped that chemistry would follow the path of progress laid down by astronomy; that when sufficient data had been assembled, a Kepler would arise and calculate the empirical laws of chemical combination, and that then a Newton would go behind these laws and discover the general principles upon which chemical attractions depended. Chemistry would then have ceased to be a mere collection of data, and would have become a mathematical science.

Dalton's atomic theory changed all this. Dalton had used the atomic theory in his work on mixed gases; and he took it sufficiently seriously to apply it to explain the laws of chemical combination in definite, multiple, and reciprocal proportions. These laws had only recently become established. When two elements combine to form only one compound, then they combine always in a fixed ratio by weight. Where two elements form two or more different compounds, then there is always a simple numerical ratio between the various weights of one element combining with a given weight of the other. And if x g of one element combine with y g of a second, and the same weight of this second element combine with z g of a third, then, if the first and third can be made to combine together, x g of the first will combine with z , or a simple multiple of z g of the third. Dalton's explanation of these laws was that every element is composed of numerous identical atoms; and that chemical combination is to be seen as the union between small numbers of these atoms. He proposed simple rules to guide chemists in determining how many atoms there were in a compound. If only one compound between two elements were known, then this compound was to be supposed to consist of one atom of each constituent; and in general the simplest possible formulae were to be employed. With the aid of these rules it was possible to calculate the relative weights of atoms.

Thus water must contain one atom of hydrogen and one of oxygen; and since it contains one part by weight of hydrogen, and seven of oxygen (using Dalton's none too accurate figures), if hydrogen be assigned unit weight, the relative weight of the oxygen atom will be seven.

In Dalton's hands the atomic theory began to be of some significance in chemistry; and there was discussion whether he was the Kepler, the Newton, or perhaps the Descartes of chemistry. One effect of this was that, whereas in 1800 chemists had probably all been atomists, in 1815 quite possibly only a minority were. Dalton's theory does not seem to have produced any sensation on its first appearance—after all, Davy was founding electrochemistry and discovering sodium and potassium at the same time—but it did at once receive substantial support from the researches of Thomson and Wollaston on oxalates. These experiments confirmed the laws of chemical combination which Dalton had set out to explain; and Wollaston wrote that they seemed to demand an atomic explanation. A few years later Thomson drew further attention to the theory in his new journal, *Annals of Philosophy*; Wollaston used it in accounting for the forms of crystals; and Berzelius, who was to become the most zealous advocate of atomism but was still at this stage unconvinced, proposed the notation which is still used in chemistry in place of the hieroglyphs of Dalton.

Thomson and Wollaston had laboured to convert Davy, in many ways the outstanding chemist of his epoch, to atomism; but their success was strictly limited. Davy accepted the laws of chemical combination, but refused to go further. And in 1814 Wollaston himself recanted. Henceforward he opposed the atomic theory in chemistry, though he actually wrote a paper trying to prove that atoms in the physical sense existed. He was famous for his accuracy and caution; and he seems to have perceived that the chemical atomic theory involved much hypothesis which was not strictly necessary, nor even very helpful. In 1814, the atomic theory only explained the laws of chemical combination, and led to the calculation of atomic weights. But similar weights, called by Wollaston 'equivalents', could be derived without hypothesis if one took the laws of chemical combination as a datum, and simply calculated what weights of various elements would combine with a given weight of oxygen. Some elements have more than one such equivalent; but the different equivalents are then always in a simple ratio. No hypothesis about the number of atoms in a compound, involving the essentially arbitrary simplicity rules, was necessary. The choice of oxygen or hydrogen as the basis of the system is of no deep significance, for the atomic weights or equivalents are all relative; hydrogen is the lightest element, but oxygen is more reactive, and occupied a central position in chemistry after the work of Lavoisier.

Wollaston's position was widely taken up. Authors of most chemistry books, especially textbooks, written in the succeeding fifty years praised Dalton for his

atomic theory, but recommended a form of it divested of all hypothesis; in other words, the laws of chemical combination and the equivalent weights based on them. When Dalton was awarded a medal by the Royal Society, some twenty years after he had published the theory, it was Wollaston's interpretation of it which Davy, the President, followed in his speech.

Chemists down to the 1860s used atomic and equivalent weights, and the terms 'atom' and 'equivalent', as synonymous; for there was no universally agreed way of deriving what we call atomic weights from equivalents. For this difficulty to be resolved, some unobjectionable method of finding the number of atoms in compounds was needed. Such a method was in fact provided by Avogadro in 1811, following on Gay-Lussac's discovery that gases combine in simple ratios by volume. Avogadro suggested that equal volumes of gases contain equal numbers of molecules, a molecule being the smallest unit of a substance that exists separately. A consequence of this hypothesis was that most elementary gases have molecules composed of two like atoms; and using it one could deduce, for example, that the simplest possible, and therefore most plausible, view of the constitution of water is that it consists of one atom of oxygen and two of hydrogen. For various reasons, Avogadro's hypothesis, though quite well known, was not accepted until after Cannizzaro had read and circulated a paper in its support at the Karlsruhe Conference in 1860. The papers by Gay-Lussac, Avogadro, and Cannizzaro are readily available in modern translations, and are not reprinted here.

Cannizzaro himself gave reasons why the hypothesis had not proved acceptable. The idea that molecules might be formed of two like atoms was repugnant to Dalton and to Berzelius, who believed, on different grounds, that like atoms must repel each other. Dalton was concerned with the mixing of unlike gases in the atmosphere. Analyses made at different heights showed that the proportion of oxygen to nitrogen was constant, though oxygen is denser than nitrogen. Dalton's solution was that oxygen atoms repelled oxygen atoms, and nitrogen nitrogen atoms; whereas atoms of different gases were indifferent to one another. Berzelius on the other hand, held an electrical theory of chemical attraction, 'dualism'. Oxygen and hydrogen atoms were held together, on this view, because the one was electrically negative and the other positive; two positive or two negative atoms could never form a stable arrangement. Dalton's difficulty disappeared when his static model of a gas was replaced by the dynamical, or kinetic, theory in which the particles were held to be in rapid motion, so that mixing would be inevitable; and Berzelius's when other forms of chemical bonding were shown to be possible, particularly in organic chemistry.

These were not the only problems. Dumas, an early supporter both of atomism and of Avogadro's hypothesis, found that they would not explain his experimental results on the vapour density of sulphur. He therefore abandoned both, exclaiming

that in chemistry it was always wrong to go beyond the facts. By 1860 his results had been accounted for; the molecules of sulphur vapour are large at low temperatures, and 'dissociate' into smaller units at high temperatures. Careful control of experimental conditions is therefore necessary to achieve consistent values for the molecular weight.

There are other methods of going from equivalent weights to atomic weights; one can use Dulong and Petit's law, which relates specific heats and atomic weights; or the law of isomorphism, which states that substances having similar crystalline form have similar formulae. But both these principles were known to have exceptions. Non-metals do not obey the law of Dulong and Petit; and one atom of potassium can replace 'ammonium', a group of five atoms, in many isomorphous salts. Nobody knew how many exceptions there might be to both laws; and so neither could be depended upon. Naturally, in these circumstances, sensible men avoided the use of atomic weights altogether, and opted for equivalents. It seems to have been impossible to write down formulae on which all chemists would agree. Some used Berzelius's symbols to stand for equivalents, others for atomic weights, and others used 'barred' atom symbols which complicated matters further; altogether, the chemistry books of the 1850s make daunting reading.

But we have outrun ourselves, and must return to Dalton and his theory. Although Davy repeated the positivistic attacks made by Wollaston, his real objection to the theory seems to have been that he considered the world to be, in the last resort, simple and harmonious. Whereas Dalton seemed to suggest that everything was made up of some forty elements—the number increased through the century—all having irreducibly different atoms, Davy clung to the corpuscularian view of Hooke and Newton that there was probably only one kind of matter. Davy's mentor had written wittily on this question in 1799: 'Whether to create a diversified system of bodies out of one, or out of a few or many elements, imply most wisdom and power, is a question which different persons would decide according to their various taste in world-making.' It is a matter of taste because on the one hand there are a considerable number of distinct atoms, and this seems far from simple; but on the other hand, the simple atoms have to be supposed to be arranged in very complex ways to generate the chemical elements. In this book, Davy and Dumas represent chemists convinced of the unity of matter. Prout is the best known exponent of this view, but his papers are readily available, and certainly no more interesting than those reprinted here.

Dalton's own ideas evolved gradually into what we think of as Daltonian atomism; but in 1810 he did declare his preference for a considerable number of genuine elements. The sense of the passage is obscured, however, by his use of 'atom' to cover both 'simple' and 'compound' particles. Compound atoms of, say,

water, are the smallest particles of it; what later generations called 'molecules'. These can be split, but then they change in character; the fragments of an atom of water are not water but oxygen and hydrogen. The simple atoms might be similarly divisible. Dalton's theory could then be interpreted as hardly a theory of matter at all; like Lavoisier's remarks on the elements, it demarcated the sphere of chemistry. That the atoms of simple bodies cannot now be split by chemical means is all that the chemist needs to know. These atoms are 'chemical atoms'; if physicists choose to theorise about particles more fundamental, then that is their affair. This attitude appears in Williamson and Kekulé, both defenders of atomism in the debates of the 1860s. The chemical atoms did not differ greatly from equivalents, but had the advantage of making it possible to talk meaningfully of different arrangements of them.

The Daltonian theory left much to be desired as a theory of matter, and physicists do not seem in general to have treated it as one. Instead they sought, in the corpuscularian tradition, simple atomic models from which the physical, and if possible in principle chemical, properties of things would follow with minimal assumptions. One such model was that of Boscovich, employed by Davy and Faraday, in which the atom became a mere point possessing inertia and surrounded by a field of force. Another was the vortex theory of William Thomson, whose atom was a whirlpool eternally swirling in the aether; this model was generally believed about 1880 to be the only one with any claim to fit all the facts. An earlier view, related to that of Boscovich but requiring more than one kind of atom, was that of Mossotti; attempts were made to apply this theory in detail, but it proved necessary to incorporate more and more hypotheses in order to do so.

Meanwhile other physicists were engaged in developing a dynamical model for a gas, whose properties were deduced from the assumption that it was composed of particles in rapid motion. The first of these theories was that of Herapath, who followed the corpuscularians in postulating hard atoms. Collisions between such bodies are extraordinarily difficult to imagine; and Herapath's successors—Waterston, Clausius, and Maxwell—employed elastic particles. With this model, once Maxwell had introduced statistical methods taken from the social sciences, it became possible to account for the gas laws, and also to predict new phenomena. In particular, Maxwell was able to derive Avogadro's hypothesis as a consequence of the dynamical theory. But elastic particles were alarming to purists; for in what could their elasticity lie? For large bodies, an atomic explanation of elasticity could be given; that the atoms were being forced closer together or further apart against repulsive or attractive forces. For atoms without parts this option was not open. It was one of the pleasing features of the vortex atom that it would be, like a smoke ring, elastic rather than hard.

In the 1860s the question of the need for an atomic theory was once again

brought to a head, this time by the publication in 1866 of the first part of Benjamin Brodie's 'Calculus of Chemical Operations'. This was an attempt to base chemistry entirely on facts, without even the possibility of hypothetical expression. Brodie provided a non-mathematical account of his work in the following year; and in the debates which followed many distinguished chemists also expressed doubts about the theory. But where Brodie thought it an incubus, to most of the other opponents it seemed a moderately useful fiction. Kekulé attempted a reply to Brodie; and two years later Williamson attempted a full-scale refutation. The debate which followed his address revealed the same deep division between the atomists and their opponents. Brodie, by his extreme positivism, the prestigious mathematics of the Calculus, and his apparent support, howbeit qualified, for believers in the unity of matter, had rallied the non-atomists. The discussion revealed the number of different positions which it is possible to take up towards theoretical entities. Brodie would have had them altogether excluded; an old-maidish attitude, we may perhaps remark, noting the barrenness of the Calculus. Others preferred, in various degrees, to use hypotheses without giving full assent to them; and some found it no more difficult to believe in atoms or an aether than in ordinary objects. Yet another attitude, owing something to romanticism, was that chemistry had taken the wrong road in becoming 'mechanical'. It should have been 'dynamical', investigating forces and energy changes, and eschewing crude atomic pictures.

Almost all this discussion soon became irrelevant, because the atomic theory suddenly began to prove very powerful. The atomic weights of Cannizzaro made possible the Periodic arrangement of the elements by Mendeléeff in 1869. And isomerism, the phenomenon of different compounds having apparently the same formulae, also proved explicable in terms of the configurations of atoms in the 1860s and 1870s. In 1864, Odling declared that isomerism was the problem of the day; ten years later, van't Hoff and Le Bel independently proposed the tetrahedral model for the valency bonds of the carbon atom. The idea of 'valency'—that elements had fixed combining powers—had been proposed in 1858 by Kekulé and Couper; and in 1865 Kekulé had suggested the ring structure for benzene. It was still possible in 1867 for Brodie to mock Kekulé's structural diagrams; ten years later they had to be taken seriously. The second part of Brodie's Calculus appeared in 1877, but he died before he could complete the work, and there is no reason to think that he saw any way of accounting for isomerism. The papers on valency and isomerism were for the most part not written in English, and translations of them are readily available; they are not, therefore, included here.

But all chemists were not convinced even by the enormously increased utility of the atomic theory. They held, as Whewell had, that the mere success of a theory is no evidence for the real existence of hypothetical entities postulated therein. The last representative of this school was perhaps Ostwald, one of the inaugurators of

the science of physical chemistry. He believed that chemistry should be based on the firm foundations of the laws of thermodynamics and not on the sands of atomism.

Meanwhile, the theories of matter of the physicists began to move closer to those of the chemists; and simultaneously chemists began to take note of physical evidence. William Thomson, to his contemporaries the outstanding physical scientist of the day, described this development; and the theme that chemists must not ignore the work of physicists runs through the Presidential Addresses of chemists at the British Association in the 1880s. Perhaps the most interesting example is that delivered by Crookes, the discoverer of cathode rays. Eighty years before, Davy had written that electricity might throw light on the ultimate constitution of matter; but his own researches with the voltaic battery had not led to any reduction in the number of chemical elements. Rather, Davy became one of the most prolific discoverers ever of new elements. Both Davy and Faraday had spoken of 'radiant matter', described by Faraday in an early lecture as a fourth state of matter. The other three were the solid, liquid and gaseous states. It is remarkable that the properties of gases are simpler than those of solids and liquids; that is, gases have many properties in common such as all obeying the gas laws. If then one could subject matter to some treatment which would get it into a fourth state, then its properties would probably be very simple indeed. The result of such an experiment might be to produce the prime matter of the corpuscularians.

Crookes, although he did not have a very exact idea of the nature of the cathode rays, believed them to be this fourth state. And Davy's prophecy was fulfilled; electricity applied to gases at low pressure did reveal the ultimate particles of bodies. For J. J. Thomson followed up Crookes' work, measuring the ratio e/m for the corpuscles, which were then identified with the units of electricity demanded to explain Faraday's laws of electrolysis, and called 'electrons'. This brings us to the story of atomic physics set out in the first volume of this series of facsimile reproductions of scientific papers; we should just notice here J. J. Thomson's remark: 'The explanation which seems to me to account in the most simple and straightforward manner for the facts is founded on a view of the constitution of the chemical elements which has been favourably entertained by many chemists: this view is that the atoms of the different chemical elements are different aggregations of atoms of the same kind.' Believers in the unity of matter could hardly be very dissatisfied with the atomic models of J. J. Thomson and Rutherford, in which all atoms were constructed of only two kinds of particle, electrons and protons. Once Daltonian atoms were seen to be thus divisible, they satisfied demands for simplicity and harmony. And Crookes had suggested an evolutionary mechanism whereby the various chemical elements might have been formed from prime matter as the Earth cooled.

In the first decade of the twentieth century, then, the atomic theory had become broadly satisfactory to believers in the unity of matter; and it was sufficiently powerful to impress, and to convince, those who in the 1860s would have treated it as a fiction useful on occasion. Positivists like Ostwald clung to the belief that nothing could establish the existence of unobservables; but he allowed himself to be convinced by the interpretation of the Brownian Motion put forward by Einstein and by Perrin. The botanist Robert Brown had given his name to the rapid to and fro motions of pollen grains suspended in water. The interpretation followed by Einstein and Perrin was that these grains danced because they were unevenly bombarded by the molecules of water in their ceaseless movement. The grains were so small that the impacts on their various sides did not all cancel out in the short run; and random motion therefore resulted. Boldly applying the kinetic theory of gases, Perrin was able to deduce from the motions of the grains values for the Avogadro number—the number of molecules in a gram-molecule—which agreed with values calculated from quite different data. The Brownian Motion thus interpreted seemed as close as could reasonably be demanded to the actual observation of molecules; and as a result very few chemists continued to withhold their assent to the atomic theory.

What then had a century of debate achieved? Chemists and physicists now had a common theory of matter, and chemistry had thereby been reduced to physics—or rather, would soon be, with the electronic theory of valency. This did not mean that chemistry ceased to exist, or simply became a branch of physics; but that it would no longer be possible for chemists to claim a complete autonomy for their science. The atomic theory of the twentieth century lent itself ultimately to mathematical treatment, and promised a genuine theoretical chemistry. While it did owe much, certainly, to Dalton, the theory which ultimately prevailed owed as much to the advocates of unity of matter. It is salutary for Englishmen to remember that the atomic theory in chemistry proved valuable only when Cannizzaro produced generally acceptable atomic weights, and when Kekulé and the organic chemists introduced the concept of valency and of directed valency bonds, giving scientific content to the idea of atoms being arranged in space. The positivists in the story might seem to have backed the wrong horse; but they forced the atomists constantly to examine, and to keep to a minimum, the assumptions and hypotheses involved in their theories. The distinction between fact and fiction in science is not as clear as Brodie tried to claim it was; but there is a distinction, and it is valuable that attention should be drawn to it, and that scientists and others should remember that theoretical entities have always a less secure status than observables.

Durham, 1967

DAVID M. KNIGHT

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Section I

THE ATOMIC THEORY IN CHEMISTRY

John Dalton's atomic theory was first described in print in Thomas Thomson's *System of Chemistry*, 3rd edition, 1807; Dalton published his own account of it in the following year. Although it is well known, it is included here because it does mark the beginning of the story. We now think of Dalton's *New System* as a work devoted to the presentation of his theory; but it is worthy of note that the first 210 pages of the book are devoted not to chemical atomic theory but to gases. The whole discussion of the atomic theory occupies only the last ten pages, where we find the simplicity rules which gave offence, the diagrams of how atoms might be arranged in space, and Dalton's atomic weights.

William Nicholson's *Journal of Natural Philosophy* was read both by amateurs and professional scientists, and articles from both groups filled its pages. For the professional, its attraction was that it provided rapid publication for short papers. In his article, Dalton was critical of the loose way in which his contemporaries used terms like 'particle'; he hoped that when proper usages could be agreed upon, the mists which enveloped the fundamental principles of the science would be dispelled. In fact, muddle persisted for another quarter of a century at least, in that the distinction between 'atom' and 'molecule' was not generally and unambiguously made. In England 'atom' was used, with various qualifying adjectives; and on the Continent, 'molecule'.

Thomas Thomson founded *Annals of Philosophy* mainly as a chemical journal, including accounts each year of the progress of the science. In the 1820s it became more geological; and finally, like *Nicholson's Journal* it became incorporated into the *Philosophical Magazine*, which has had a distinguished history and still continues. It was Thomson more than anybody else who made Dalton's theory well known, in his textbook and in this paper; the second half of which—a table of atomic weights—has been omitted. Later Thomson brought Prout's hypothesis to the attention of the scientific world; he is remembered for these popularisations and for his *History of Chemistry*.

William Hyde Wollaston was one of the outstanding scientists of the day, who made his fortune by his discovery of how to work platinum, which became widely used for chemical apparatus—its application to jewellery came much later. Wollaston investigated topics as diverse as fairy rings, seasickness, and why the eyes in portraits seem to follow one around. He also invented the goniometer, a device for measuring the angles of crystals; and in the paper reproduced here he sought to show how from atoms of spherical, or spheroidal, form, the various crystal structures might be built up. The wooden balls he used are on view at the Science Museum, South Kensington.

Jons Jacob Berzelius was perhaps the most important chemist of the second and third decades of the century. He took up Davy's idea that chemical bonding was electrical, and Dalton's atomic theory, and built them into a system which he called 'dualism'. He transformed chemistry into a science based upon exact data with his determinations of atomic weights. And he was responsible for training many of the most distinguished chemists of the next generation. In this paper, Berzelius had not yet accepted atomism, preferring to base weights on combining volumes of gases; but he proposed the notation still used today to signify atoms in place of Dalton's pictures, which were inconvenient in use.

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CHAP. III.

ON CHEMICAL SYNTHESIS.

WHEN any body exists in the elastic state, its ultimate particles are separated from each other to a much greater distance than in any other state; each particle occupies the centre of a comparatively large sphere, and supports

its dignity by keeping all the rest, which by their gravity, or otherwise are disposed to encroach up it, at a respectful distance. When we attempt to conceive the *number* of particles in an atmosphere, it is somewhat like attempting to conceive the number of stars in the universe; we are confounded with the thought. But if we limit the subject, by taking a given volume of any gas, we seem persuaded that, let the divisions be ever so minute, the number of particles must be finite; just as in a given space of the universe, the number of stars and planets cannot be infinite.

Chemical analysis and synthesis go no farther than to the separation of particles one from another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce, consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance.

In all chemical investigations, it has justly been considered an important object to ascertain the relative *weights* of the simples which

constitute a compound. But unfortunately the enquiry has terminated here ; whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms of the bodies might have been inferred, from which their number and weight in various other compounds would appear, in order to assist and to guide future investigations, and to correct their results. Now it is one great object of this work, to shew the importance and advantage of ascertaining *the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.*

If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple : namely,

- 1 atom of A + 1 atom of B = 1 atom of C, binary;
- 1 atom of A + 2 atoms of B = 1 atom of D, ternary.
- 2 atoms of A + 1 atom of B = 1 atom of E, ternary.
- 1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
- 3 atoms of A + 1 atom of B = 1 atom of G, quaternary.
- &c. &c.

The following general rules may be adopted as guides in all our investigations respecting chemical synthesis.

1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary.

2d. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.

3d. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.

4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, &c.

5th. A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients.

6th. A *ternary* compound should be specifically heavier than the mixture of a *binary* and a simple, which would, if combined, constitute it; &c.

7th. The above rules and observations equally apply, when two bodies, such as C and D, D and E, &c. are combined.

From the application of these rules, to the chemical facts already well ascertained, we

deduce the following conclusions; 1st. That water is a binary compound of hydrogen and oxygen, and the relative weights of the two elementary atoms are as 1 : 7, nearly; 2d. That ammonia is a binary compound of hydrogen and azote, and the relative weights of the two atoms are as 1 : 5, nearly; 3d. That nitrous gas is a binary compound of azote and oxygen, the atoms of which weigh 5 and 7 respectively; that nitric acid is a binary or ternary compound according as it is derived, and consists of one atom of azote and two of oxygen, together weighing 19; that nitrous oxide is a compound similar to nitric acid, and consists of one atom of oxygen and two of azote, weighing 17; that nitrous acid is a binary compound of nitric acid and nitrous gas, weighing 31; that oxynitric acid is a binary compound of nitric acid and oxygen, weighing 26; 4th. That carbonic oxide is a binary compound, consisting of one atom of charcoal, and one of oxygen, together weighing nearly 12; that carbonic acid is a ternary compound, (but sometimes binary) consisting of one atom of charcoal, and two of oxygen, weighing 19; &c. &c. In all these cases the weights are expressed in atoms of hydrogen, each of which is denoted by unity.

In the sequel, the facts and experiments from which these conclusions are derived, will be detailed ; as well as a great variety of others from which are inferred the constitution and weight of the ultimate particles of the principal acids, the alkalis, the earths, the metals, the metallic oxides and sulphurets, the long train of neutral salts, and in short, all the chemical compounds which have hitherto obtained a tolerably good analysis. Several of the conclusions will be supported by original experiments.

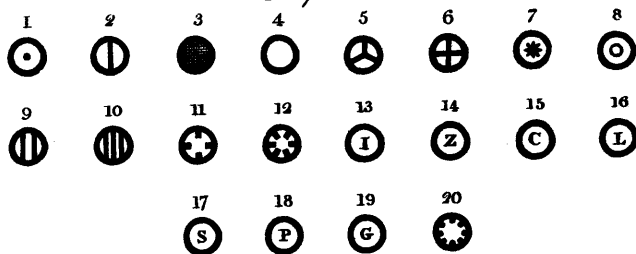
From the novelty as well as importance of the ideas suggested in this chapter, it is deemed expedient to give plates, exhibiting the mode of combination in some of the more simple cases. A specimen of these accompanies this first part. The elements or atoms of such bodies as are conceived at present to be simple, are denoted by a small circle, with some distinctive mark ; and the combinations consist in the juxta-position of two or more of these ; when three or more particles of elastic fluids are combined together in one, it is to be supposed that the particles of the same kind repel each other, and therefore take their stations accordingly.

END OF PART THE FIRST.

ELEMENTS

Plate 4.

Simple



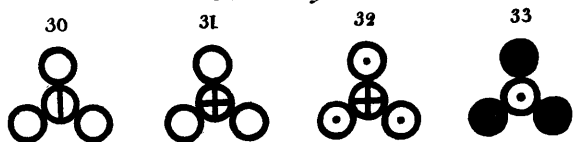
Binary



Ternary



Quaternary



Quinquenary & Sextenary



Septenary

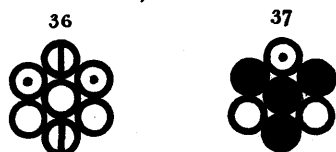
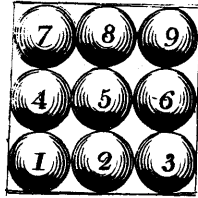
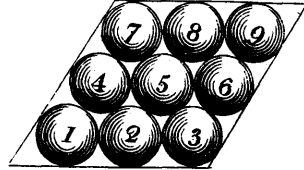


Plate. 3.

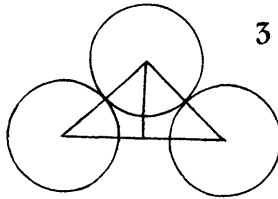
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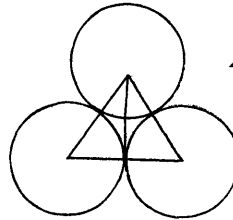
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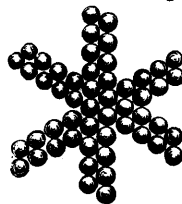
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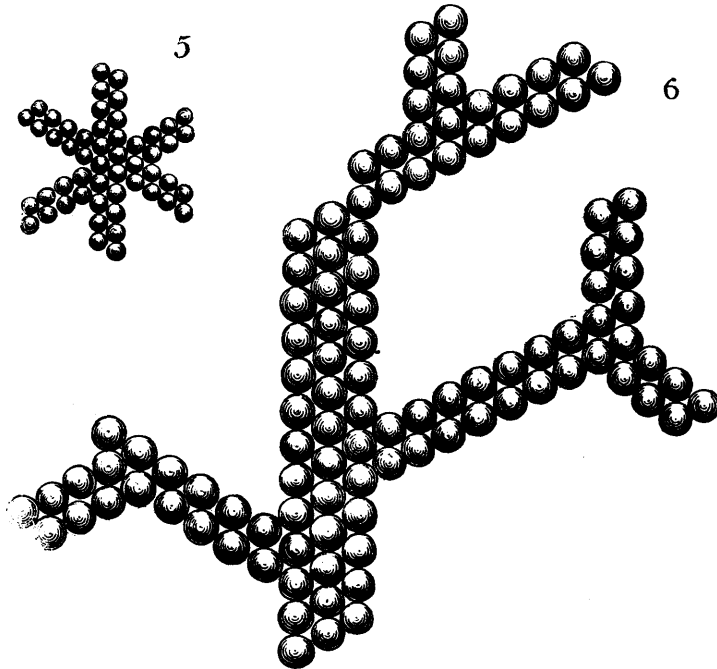


PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.		Fig.	
1	Hydrog. its rel. weight 1	11	Strontites - - - 46
2	Azote, - - - - 5	12	Barytes - - - - 68
3	Carbone or charcoal, - 5	13	Iron - - - - 38
4	Oxygen, - - - - 7	14	Zinc - - - - 56
5	Phosphorus, - - - 9	15	Copper - - - - 56
6	Sulphur, - - - - 13	16	Lead - - - - 95
7	Magnesia, - - - - 20	17	Silver - - - - 100
8	Lime, - - - - 23	18	Platina - - - - 100
9	Soda, - - - - 28	19	Gold - - - - 140
10	Potash, - - - - 42	20	Mercury - - - - 167

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight = - - - - 8
22. An atom of ammenia, composed of 1 of azote and 1 of hydrogen - - - - 6
23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen - - - - 12
24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen - - - - 6
25. An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen - - - - 12
26. An atom of nitrous oxide, 2 azote + 1 oxygen - 17
27. An atom of nitric acid, 1 azote + 2 oxygen - 19
28. An atom of carbonic acid, 1 carbone + 2 oxygen 19
29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen - - - - 7
30. An atom of oxynitric acid, 1 azote + 3 oxygen 26
31. An atom of sulphuric acid, 1 sulphur + 3 oxygen 34
32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen - - - - 16
33. An atom of alcohol, 3 carbone + 1 hydrogen - 16
34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas - - - - 31
35. An atom of acetous acid, 2 carbone + 2 water - 26
36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water - - - - 33
37. An atom of sugar, 1 alcohol + 1 carbonic acid - 35

220 EXPLANATION OF THE PLATES.

Enough has been given to shew the method; it will be quite unnecessary to devise characters and combinations of them to exhibit to view in this way all the subjects that come under investigation; nor is it necessary to insist upon the accuracy of all these compounds, both in number and weight; the principle will be entered into more particularly hereafter, as far as respects the individual results. It is not to be understood that all those articles marked as simple substances, are necessarily such by the theory; they are only necessarily of such weights. Soda and Potash, such as they are found in combination with acids, are 28 and 42 respectively in weight; but according to Mr. Davy's very important discoveries, they are metallic oxides; the former then must be considered as composed of an atom of metal, 21, and one of oxygen, 7; and the latter, of an atom of metal, 35, and one of oxygen, 7. Or, soda contains 75 per cent. metal and 25 oxygen; potash, 83.3 metal and 16.7 oxygen. It is particularly remarkable, that according to the above-mentioned gentleman's essay on the Decomposition and Composition of the fixed alkalies, in the Philosophical Transactions (a copy of which essay he has just favoured me with) it appears that "the largest quantity of oxygen indicated by these experiments was, for potash 17, and for soda, 26 parts in 100, and the smallest 13 and 19."

DIRECTIONS TO THE BINDER.

Plate 1 to face page 217.

2 to face page 218.

3 to follow plate 2.

4 to face page 219.

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AND
THE ARTS.

FEBRUARY, 1811.

ARTICLE I.

Inquiries concerning the Signification of the word Particle, as used by modern Chemical Writers, as well as concerning some other Terms and Phrases. By Mr. JOHN DALTON. In a Letter from the Author.

To Mr. NICHOLSON.

SIR.

IN perusing the modern books, which are edited under the titles of Elements or Systems of Chemistry, I have been greatly perplexed in endeavouring to understand the meaning, which the authors attach to certain words and phrases, which are of perpetual occurrence, particularly when treating of *affinity*, but which the authors nowhere define. I allude more especially to the word *particle*. Meaning of chemical terms undefined.

With respect to the article *affinity* itself it is somewhat remarkable, that different authors should view it in such different lights. Lavoisier in his Elements of Chemistry does not say a word on the subject, except a few observations in his preface tending to show the difficulties of it, and its unsuitness to be presented to a novice in chemistry. In Vol. XXVIII. No. 127—FEB. 1811. G speak-

speaking of the number and nature of elements, he says, "I shall therefore only add on this subject, that, if by the term *elements* we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable we know nothing at all about them." Chaptal employs about 20 pages on affinity, two on the affinity of aggregation, and the rest on the affinity of composition. In the third edition of your First Principles of Chemistry, I observe 10 pages on affinity. Berthollet has written a small volume on the subject. Fourcroy, Thomson, Murray, and Henry, have all expanded their views on this subject pretty extensively. From these observations it should seem, that the article *affinity* in systems of chemistry has been of *growing* importance since the time of Lavoisier's publication. This may certainly be right; but as the subject is acknowledged to be one of the most difficult in the science, it is highly necessary, that authors should treat it with all the perspicuity of which it is capable; the terms used should be clear and well defined; metaphorical expressions should be avoided; and ambiguities should be guarded against with all possible care.

Chaptal. Chaptal has been very sparing in the use of the term *particle* when treating of affinity (I refer to your translation, 2d ed.); he only mentions it three times, twice unqualified, and once along with the epithet *elementary*; he seems to use *integrant part*, where others would use *particle*, and he defines it thus: "two drops of water, which unite together into one, form an aggregate, of which each drop is known by the name of an integrant part."

Nicholson's First Principles. On the subject of affinity I observe you use the term *particles* frequently, but only once in the singular number. No definition of it is ever given; but the last time it occurs is in a very judicious concluding remark, which I do not remember to have seen in any subsequent writer; namely, "it seems reasonable to infer, that two compounded particles coming together by attraction, undisturbed by any other cause, should dispose themselves so as to apply such sides of each together, as are occupied by principles the most attractive of each other." In another part of the chapter you observe, that "the minutest parts, into which
an

an aggregate can be *imagined to be* divided without decomposition, are called integrant parts; but the parts into which it is divided by decomposition are called component parts or principles." These definitions would be clear and intelligible to me, if the words I have put in italics were omitted*; the sense affixed to *integrant parts* is better than that of Chaptal, and is the same as the most correct modern writers apply to *integrant parties*. But, after thus defining the terms *integrant parts*, I do not find, that you have again used them throughout the chapter.

Integrant and component parts.

From the high encomiums, which several modern writers pass on Berthollet's researches into the laws of chemical affinity, I was induced to hope, that in a volume written exclusively upon affinity by so able a hand, I should find the term *particle* clearly defined in the first page. I took up the English translation, and read 37 pages without once meeting with the word *particle*, or any other word of similar import. I was beginning to think, that the author intended to abolish the old doctrine of bodies consisting of extremely small parts bound together by a principle of cohesion, or affinity of aggregation, and to establish the one that bodies consist entirely of cohesion, when in the opening of the 5th article I read, "the cohesion of the moleculæ of a body is due to the reciprocal affinity of these moleculæ;" the word moleculæ did not again occur in the volume to my cursory observation. In the same page I met with the phrase *integral parts*, and afterward in the space of 150 pages the words *part* and *particle* were observed in about a dozen places. Whatever obscurity may be found in Berthollet's researches then, they do not arise from the frequent use of the term *particle*.

Berthollet on chemical affinity.

Moleculæ.

* I do not know how Mr Dalton would understand the passage, if the words in italics were omitted; but they appear necessary, to express the true meaning with precision. Suppose a single atom of sulphuric acid combines with a single atom of mineral alkali to form a particle of sulphate of soda, and a crystal to be formed by the aggregation of such particles; we cannot actually divide it into these component parts, though we can imagine it so divided. The word *imagined* may be here taken as synonymous with the word *conceived* of the geometers, and has no necessary relation to operative or human practicability. N.

Dr Thomson
on affinity.

Dr. Thomson, in a short essay on affinity in general, uses the term *particle* frequently, and without any direct definition; but as he advances his idea of *particle* is gradually developed. Indeed he is almost the only writer, who has courage to talk of *a particle, two particles, &c.* *Homogeneous* particles are those of the same body; *heterogeneous* particles those of different bodies; thus "a particle of iron and a particle of lead are heterogeneous." Again, "an integrant particle of water is composed of particles of hydrogen and oxygen urged towards each other, and kept at an insensible distance, by heterogeneous affinity; and a mass of water is composed of an indefinite number of integrant particles of that fluid, urged towards each other by homogeneous affinity." He supposes the particles of matter to have figure and magnitude, and adds, "if the particles of bodies have length, breadth, and thickness, we cannot avoid conceiving them as composed of an indeterminate number of still more minute particles or atoms. Now the affinity of two integrant particles for each other must be the sum of the attractions of all the atoms in each of these particles for all the atoms in the other," &c. Here the meaning of a *particle* is very clearly pointed out. Bodies, such as iron, are constituted of *particles* connected together by homogeneous affinity; these particles are each of them constituted of a certain unknown number of subordinate particles, which last are the atoms or ultimate particles, into which the body is capable of being resolved without decomposition. This notion is clear as far as it goes (I mean not as to its truth, but as to the expression); it would seem however to require something to be said about the *cohesion* of the atoms to form a particle, namely, whether it is the same or different from the cohesion of the particles to form a mass; in other words, whether the force of cohesion, which binds together the atoms or first order of particles, is the same as that which binds the second order of particles. See Thomson's Chemistry, 3d ed. vol. iii.

Murray's Chemistry.

Mr. Murray uses the term *particles* frequently; he commences his work with the observation, that "all the phenomena of chemistry arise from the attractions and repulsions exerted between the particles of matter;" but I have not been

been so fortunate as to meet with his definition of the unqualified term *particle*. He has however given the best definition I have yet seen of *integrant particles*. "The calcareous spar, to take it as an example, may be reduced to a particle, beyond which the division cannot be carried without resolving it into its elements, lime and carbonic acid; or, at least, it may be reduced to a particle, beyond which, if its minuteness allowed us to operate upon it, it is demonstrable its figure would not change. To these last particles, the result of the mechanical analysis, Haüy gives the name of *integrant particles*, and their union constitutes the crystal." See Chemistry, 1st edit. vol. i, page 56. Again, on *integrant* and *constituent* particles, "the constituent or component parts are substances differing in their nature from each other, and from the substances they form. The integrant parts are precisely similar to each other, and to the general mass, which is composed by their union; or they are *merely* the smallest particles into which a substance can be resolved without decomposition; while decomposition is always implied in the division of a body into its constituent particles. The integrant parts are united by the force of aggregation, the constituent parts by chemical affinity," &c. All this is more than perspicuous; it is excellent; and from the familiar manner in which Mr. Murray introduces "the smallest particles, into which a substance can be resolved without decomposition," and from the precise definition of them, one would be inclined to believe the author was going to say something more about them in the sequel; but he scarcely mentions them again, while the unqualified term *particles* is perpetually introduced.

Dr. Henry adopts the common distinction of the attraction of aggregation, and that of composition, or affinity. Henry's Chemistry. "In simple bodies, therefore, the cohesive affinity alone is exerted; but compounds are influenced by both affinities, their *constituent* or dissimilar parts being united by chemical affinity, and their *integrant* or similar parts by the affinity of aggregation." Chemistry, 6th ed. vol. i, page 52. He does not however clearly define *integrant parts*; it is not sufficient to say, that "a lump of copper may be considered

as composed of an infinite number of minute particles or integrant parts, each of which has precisely the same properties as those that belong to the whole mass." For, it is obvious, such *integrant parts* may either be Dr. Thomson's *particles* (of the first order) or Mr. Murray's smallest particles into which a substance can be resolved without decomposition, which I call atoms. Dr. Henry uses the term *particles* at times in the same indefinite manner as his predecessors.

Words improperly used.

Ratio.

There are some other current expressions among chemical writers on affinity, that are either erroneous or misunderstood. Chaptal says, that "the affinity of composition is in the inverse ratio of the affinity of aggregation." Dr. Henry has adopted a similar expression, page 53. The only thing that can be intended by this expression is, that the affinity of composition is less efficacious, as the affinity of aggregation is greater; but not the affinity has precisely *half* the effect, when that of aggregation is *double*.

Berthollet on the effect of quantity on affinity,

Some new opinions and expressions were introduced by Berthollet, which want both confirmation and illustration; one of them is, that the effect of affinity is in proportion to the weight of a body multiplied by the degree of its affinity. Mr. Murray, page 85, has it: "the chemical action of any body is exerted in the ratio of its affinity and quantity." Dr. Henry observes, page 72, "to obtain a measure of the action of two bodies on a third, if their respective affinities were precisely determined, it would only be necessary to multiply the number indicating the affinity by the quantity." Berthollet's language on this subject would seem to warrant this conclusion as his; but the experiments he adduces certainly warrant no more than that the effect "is modified considerably by the mass," as Dr. Thomson expresses it. Mr. Murray however has attempted to illustrate the *truth* of the principle (Appendix, page 19), and Dr. Henry to explain its *meaning* (page 72), according to the sense in which they understand it. The latter has succeeded very well; but the former, having a much more difficult task, has, I think, still left some obscurity about it. The explanation is this: "if a particle of sulphate of barytes be on every side in contact with particles of potassia, what

what additional force can be gained from an additional quantity of potassia, which must be without the sphere of action?" This is a very proper statement of the question. I wish the author had kept closely to it, and not substituted for it another and more complex one. Mr. M. continues: "this objection however may be obviated, by considering the manner in which quantity operates. Suppose two bodies, A and B, to be presented to each other, the particles of each within the requisite distance will combine together in that proportion, in which they will be mutually saturated. Suppose it to be the one which is in larger proportion; its mass will continue to operate, and, even if there be no successive application of it to B, from the motion attending the combination, its uncombined or unsaturated particles will take *part of the particles* of B which have entered into the combination; so that the *whole particles* of B which have been attracted by A, instead of remaining combined with part of it, in the proportion in which saturation takes place, will be diffused through the mass; and hence by an increase in this mass there will be an addition to the force of affinity." Mr. M. then adds, "no law with regard to chemical affinity is more important than that now illustrated." But the illustration is almost lost upon me, for want of knowing the precise meaning of *particle*.

Another of Berthollet's observations is, "that the action of a substance, which tends to decompose a combination, diminishes in proportion as its saturation advances; for this substance may in such case be considered as composed of two parts, one of which is saturated, and the other free. The former may be considered as inert, and as unconnected with the latter, the quantity of which diminishes according as the saturation advances; while on the contrary the action of that which has been eliminated increases in proportion to the augmentation of its quantity, until the equilibrium of the contending forces ends the operation, and limits the effect." Researches, page 15. I apprehend it is to this that Mr. Murray alludes, page 82, when he deduces the law, "that the force of attraction is in the inverse ratio of saturation, or that the particles which enter first into combination are retained by a stronger affinity than those afterward

and on that of
the progress of
saturation.

Here mistaken
by his com-
mentators.

His meaning
explained.

ward combined;" and Dr. Henry, page 73, when he says, "the force of affinity is in the inverse proportion of neutralization." This principle Dr. H. explains numerically by supposing 100 parts of potash to be divided into portions, and successively put into sulphuric acid, the first portion, he argues, will be held more forcibly than the second, &c. Now whatever errors Mr. Berthollet may have fallen into, I think he cannot be fairly charged with this; his commentators here appear to me to be responsible. Suppose, instead of potash, barytes is substituted; would these gentlemen say, Berthollet maintains the first formed sulphate of barytes would be with more difficulty decomposed than the last formed? I think no such inference can be fairly drawn from his position. If I understand Berthollet, he means, that, if a combination, as sulphate of potash, have another substance put to it, tending to decompose the combination, as barytes, the action of the barytes will be less and less powerful as the decomposition goes forward; the great quantity of potash liberated will lend its assistance to that still in combination, and both finally will prevent the small quantity of barytes remaining from effecting a complete decomposition of the sulphate of potash.

I would not have it to be understood, that by these inquiries I wish to depreciate your publication on chemistry, or those of the ingenious gentlemen whom I have had occasion to mention. The works have their excellencies; and if they should also have their defects, it is of interest to the public and to the authors to be made acquainted with them. I hope either you, or some of your readers, will undertake to explain what you conceive chemical authors signify by *particles*; and then I think we shall be enabled soon to dispel the mists, that envelope the fundamental principles and operations of the science.

I am yours,

J. DALTON.

Manchester, Dec. 19th.

II.

ARTICLE IX.

On the Daltonian Theory of Definite Proportions in Chemical Combinations. By Thomas Thomson, M.D. F.R.S.

I PROMISED in an early number of the *Annals of Philosophy* some observations on Mr. Dalton's theory of definite proportions, and I now sit down to fulfil that promise. Too much attention cannot be paid to this important theory, the developement of which I consider as the greatest step which chemistry has yet made as a science. It puts us in the way of establishing principles of rigid accuracy as the foundation of our reasoning, and to call in the assistance of mathematics to promote the progress of a science which has hitherto eluded the aid of that unrivalled instrument of improvement. The idea of definite proportions seems to have struck the mind of Richter, though the methods which he took to determine them were far from successful ; and Mr. Higgins, in his work on phlogiston, maintained the opinion that chemical bodies unite atom to atom. But the generalization of the doctrine, and the striking and irresistible proofs deduced from the combinations of the simple substances, and the acids

and bases belong entirely to Mr. Dalton ; without whose labours the theory would probably have still remained unknown. On the Continent the notions originally established by Dalton have been adopted, and ingeniously extended in certain cases by Gay-Lussac ; and Berzelius has published a most elaborate, extensive, and accurate set of experiments on the same subject, which fully confirm the Daltonian doctrine, while he has deduced several subordinate laws from his analyses, which, though in some measure empirical, are nevertheless of very considerable importance in determining the constitution of bodies.

In this country less attention has hitherto been bestowed upon Dalton's theory than could have been anticipated from the sagacity and enlightened views of many of our chemists. Dr. Bostock has even written an essay against it ; but from the well-known candour and liberality of this able philosopher, I have no doubt that he will embrace it with ardour as soon as his doubts are removed. Sir Humphry Davy has embraced the Daltonian theory with some modifications and alterations of terms ; but his notions are not quite so perspicuous as those of Mr. Dalton, and they do not appear to me so agreeable to the principles of sound philosophy. These, as far as I recollect, are the only chemists in this country who have written upon the subject (some observations of Dr. Wollaston, and of myself, excepted) ; though not the only persons who have embraced the opinions of Mr. Dalton. I shall in this essay state, in the first place, the nature of the theory, and the grounds upon which it has been advanced ; in the second place, I shall state the laws, or subordinate canons, which have been deduced from analysis, in consequence of the introduction of this theory ; and in the third place, I shall give a table of the numbers representing the proportions in which substances combine, deduced from the application of the Daltonian theory to the most accurate analyses hitherto made.

I. *Outline of the Daltonian Theory.*

It may be necessary to mention in the outset that I propose to give the view which I have been accustomed myself to take of the subject, and that I would not be understood to make Mr. Dalton answerable for the opinions which I shall state. I call it the Daltonian theory because I consider it as belonging to Mr. Dalton ; because he first suggested it to me, and set me to think on the subject ; and, of course, every thing here stated originated from him, either directly, or at least indirectly.

1. With respect to the nature of the ultimate elements of bodies, we have no means of obtaining accurate information ; but it is the general opinion that they consist of *atoms*, or minute *solids*, incapable of farther division. That these *atoms* are mere mathematical points surrounded with spheres of attraction and

VOL. II. N° I.

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repulsion, as Buscovich supposed, appears to me incomprehensible. They must, I think, be physical points, as minute as you will, but still possessed of length, breadth, and thickness. This opinion, I say, is generally received by philosophers; and I cannot, for my part, conceive any other. It is taken for granted as the foundation of the Daltonian theory; and, I presume, will be readily admitted by every one without hesitation.

2. In cases of the chemical union of one body with another, the substances combined are dispersed every where through the whole mass. Thus chalk is a compound of lime and carbonic acid. Now how minute a portion soever of chalk we take, we shall find it to contain both lime and carbonic acid. How minute a portion soever of water we take, we shall find it to contain both oxygen and hydrogen. How minute a portion soever of saltpetre we examine, we shall find it to contain both nitric acid and potash. Now this could not be the case unless the atoms of the combining bodies united with each other. This accordingly is the opinion universally entertained respecting chemical combinations. It has been long generally admitted, and does not therefore require any farther illustration.

3. All chemical compounds contain the same constant proportion of constituents with the most rigid accuracy, no variation whatever ever taking place. Water is universally composed of 1 part of hydrogen and 7.5 parts of oxygen; sulphuric acid, of 1 part of sulphur and 1.5 part of oxygen; carbonic acid, of 1 part of carbon and 2.7 parts nearly of oxygen, by weight. This permanency of chemical compounds is generally admitted. Indeed, the whole science of chemistry is founded on it, and depends upon it. Even Berthollet, who contends for indefinite proportions in the abstract, admits the incontrovertible fact that the proportions of chemical combinations in general are permanent.

4. This permanency of chemical compounds cannot be owing to any thing else than to the union of a certain determinate number of the atoms of one constituent with a certain determinate number of the atoms of the other. Let us suppose water the compound. Let the number of atoms of oxygen which unite be x , and of hydrogen y , then an integrant particle of water will in every case be $x + y$.

5. Oxygen has the property of uniting with different bases in various proportions, sometimes in two, sometimes in three, four, or even six proportions with the same base. Thus with azote it unites in four proportions, with carbon in two, with mercury in two, and so on. Now if we represent the weight of base with which the oxygen unites by a , and suppose all the different proportions of oxygen to unite with this portion of base; and if we denote the first portion of oxygen by b ; then, in general, the

constituents of the different compounds formed by the union of the different doses of oxygen with the base will be as follows:—

- 1st compound, $a + b$
- 2d compound, $a + 2b$
- 3d compound, $a + 3b$
- 4th compound, $a + 4b$

Suppose 10 parts of oxygen enter into the first compound, then 20 parts enter into the second compound, 30 parts into the third compound, and 40 parts into the fourth compound. Hence, whatever number of atoms of oxygen enter into the first compound, twice that number enters into the second, thrice into the third, and four times that number into the fourth.

Hence it is clear that there is a determinate number of atoms of oxygen which always enter into these combinations. If we represent this number by x , then $a + x$ is the first compound, $a + 2x$ the second, $a + 3x$ the third, and $a + 4x$ the fourth. Now it would be singular if 2, 3, 4, &c. atoms of oxygen were to be always inseparably linked together, so as never to be able to enter into combinations separate. It is much more simple to conceive that x represents only one atom. Even though the opinion should not be mathematically true, still it would be proper to adopt it: for as far as our calculations are concerned, a number of atoms of oxygen constantly and invariably united constitute a compound atom, about which we may reason as accurately and justly as we could about the simple atoms themselves. Indeed, I think that x certainly represents one atom only; for oxygen gas being a permanently elastic fluid, must consist of atoms that repel each other. Hence I conceive that a compound atom of oxygen, or a number of atoms of it united together, is impossible. And if x consisted of atoms not united together, I can see no reason why the same number should unite in every case (or a multiple of it) with other bodies.

This reasoning may be applied to hydrogen as well as oxygen. Hydrogen has the property of uniting in different proportions with various bodies, as with carbon, phosphorus, sulphur, &c. In these different proportions we find the hydrogen always denoted by y , $2y$, &c. Hence we have every reason to conclude that y , which represents the proportion of hydrogen which unites with the other constituent in these cases is an *atom*.

The numbers x and y are easily discovered, by making an accurate analysis of the different compounds into which various proportions of oxygen and hydrogen enter, and when reduced to their lowest terms they are very nearly $x = 7.5$ and $y = 1$. Hence these numbers represent the ratios of the weight of an atom of oxygen and an atom of hydrogen to each other. Now it deserves attention that these numbers represent the composition of water.

For it has been ascertained, I think, with precision, that water is composed of 100 measures of oxygen gas, and 200 measures of hydrogen gas. Now the specific gravity of these gases are as follows :—

Oxygen	1·104
Hydrogen	0·073

Hence water is composed by weight of

Oxygen	7·56
Hydrogen	1·00

From this coincidence we are entitled to conclude that water is formed by the union of an atom of oxygen to an atom of hydrogen. This very important conclusion is supported by other considerations. Oxygen and hydrogen have never been made to combine in any other proportion than that in which they exist in water. Hence this proportion must be that which unites most readily, and with the greatest force. Now as the atoms of hydrogen repel each other, as is the case also with the atoms of oxygen; and as hydrogen is attracted by oxygen; it is obvious that when they are mixed equably, as is the case when 200 measures of hydrogen gas, and 100 measures of oxygen gas, are put into a tube, and fired by electricity, they will most readily unite atom to atom. This, though not in itself decisive, is a corroborating circumstance. It follows from it that a given bulk of hydrogen gas contains only one-half the number of atoms that exist in the same bulk of oxygen gas.

6. Knowing the weight of an atom of oxygen and of an atom of hydrogen, we have it in our power to determine the weight of an atom of the other substances which unite with oxygen, or with hydrogen, or with both. For example, 100 parts of sulphur unite with two proportions of oxygen, the first consisting of 100, the second of 150 parts, both in weight. Here the proportions of oxygen being to each other as the numbers 1, $1\frac{1}{2}$, or as 2, 3, it is reasonable to suppose that the first portion represents two atoms of oxygen, and the second three atoms; and that there is another compound, consisting of sulphur united with one atom of oxygen, not yet discovered. If this supposition be reasonable, it follows, that the weight of sulphur which enters into these combinations represents an atom of that substance. Therefore 100 represents an atom of sulphur, and 100 two atoms of oxygen; so that an atom of sulphur, it appears, is just double the weight of an atom of oxygen.

We have it in our power to verify this reasoning, by means of the combinations which sulphur makes with hydrogen. It has been ascertained that 100 measures of hydrogen gas, when they unite with sulphur, do not alter their bulk, but merely their

1813.] *Definite Proportions in Chemical Combinations.* 37

specific gravity. Hence, in order to determine the constituents of sulphureted hydrogen gas with perfect accuracy, we have only to ascertain correctly the specific gravity of hydrogen gas and of sulphureted hydrogen gas. Now

100 cubic inches of hydrogen gas weigh 2·230 gr.
100 cubic inches of sulphureted hydrogen . . . 35·890

Hence it follows that sulphureted hydrogen gas is composed of

Hydrogen	2·23	or	1·00
Sulphur	33·66		15·09

This shows us that if sulphureted hydrogen gas is composed of an atom of hydrogen united to an atom of sulphur (and hardly any other supposition seems admissible), then if an atom of hydrogen weigh 1, an atom of sulphur will weigh 15·09. The combination of oxygen and sulphur gave us 15·12 for the weight of an atom of sulphur. Thus the two processes of reasoning lead to the same conclusion, since the difference between 15·09 and 15·12 is only $\frac{3}{1000}$. This is as near a coincidence as it is possible to obtain from chemical experiments, where absolute precision, from the nature of our processes, is impossible.

By a similar mode of reasoning, we may determine with considerable accuracy the weight of an atom of azote, phosphorus, carbon, and the metals. It would be tedious to state the methods here at full length; but some of the most important of them will be given afterwards.

It is hardly necessary to observe, how very powerfully a particular conclusion is confirmed when we arrive at it by different processes. This advantage we have in full perfection when we set about determining the weight of the atoms of the simple substances. In most cases we come to the same conclusion by two, three, or four different methods. These coincidences, I think, could not exist, unless the conclusion were well founded.

7. I shall terminate this part of the subject with Mr. Dalton's canons for the combination of the atoms of bodies with each other. They are very ingeniously contrived, and their truth, I conceive, will be readily admitted by every person who pays due attention to the subject:—

1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary** one, unless some cause appear to the contrary.

2d. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.

* By *binary*, Mr. Dalton means a compound of one atom of one body with one atom of another; by *ternary*, a compound of one atom of one body with two atoms of another; and so on.

3. When three combinations are observed, we may expect one to be *binary*, and the other two *ternary*.

4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, &c.

5th. A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients.

6th. A *ternary* compound should be specifically heavier than the mixture of a *binary* and a simple, which would, if combined, constitute it, &c.

7th. The above rules and observations equally apply, when two bodies, such as C and D, D and E, &c. are combined.*

If the observations of Gay-Lussac be correct, nitrous gas constitutes an exception to Mr. Dalton's 5th rule. It will come under our examination hereafter.

II. *Chemical Canons founded on the above Theory, but deduced from Analysis.*

1. When gaseous bodies combine they always unite in determinate proportions; and if we represent the bulk of the gas that enters into the compound in the smallest quantity in bulk by 1, then the bulk of the other constituent is either 1, 2, or 3. Thus muriate of ammonia is composed of 1 muriatic acid + 1 ammonia in bulk; carbonate of ammonia, of 1 carbonic acid + 1 ammonia; nitrous gas, of 1 azote + 1 oxygen; water, of 1 oxygen + 2 hydrogen; gaseous oxide of azote, of 1 oxygen + 2 azote; nitrous acid, of 1 azote + 2 oxygen, or of 1 oxygen + 2 nitrous gas; sulphuric acid, of 1 oxygen + 2 sulphurous acid; carbonic acid, of 1 oxygen + 2 oxide of carbon; ammonia, of 1 azote + 3 hydrogen; nitrous acid gas, of 1 oxygen + 3 nitrous gas. This canon has been established by Gay-Lussac, I think, in a satisfactory manner.† The only one of his conclusions which is still doubtful is that nitrous acid is a compound of 2 nitrous gas + 1 oxygen gas. At least I have not been able to make the two gases unite exactly in that proportion. This canon is obviously connected with the Daltonian theory. It is simple and beautiful, and of considerable utility in practical chemistry.

2. The quantity of acid requisite to saturate the different metals is directly as the quantity of oxygen which these metals require to convert them into oxides. Thus 100 parts of mercury require 4.16 parts of oxygen, and 100 parts of silver require 7.9 parts of oxygen, to convert them into oxides. Therefore the quantity of acid necessary to saturate 100 parts of mercury

* Dalton's New System of Chemistry, vol. i. p. 214.

† Mem. d'Arcueil, vol. ii. p. 207.

is to the quantity necessary to saturate 100 parts of silver as the number 4.16 to 7.9. This law was first pointed out by Gay-Lussac.* It may be expressed in the following manner, which adapts it better to the purposes of the chemist. When different metallic oxides saturate the same weight of acid, each contains exactly the same weight of oxygen. According to Berzelius, in order to saturate 100 parts of muriatic acid, a metal must be combined with 42 parts of oxygen; to saturate 100 of sulphuric acid, it must be combined with 20 parts of oxygen.

I believe that this law applies only to those metals which are precipitated by each other; namely, gold, silver, mercury, copper, lead, cobalt, and perhaps iron, zinc, and one or two others. The other metals, I conceive, follow a different law; and it is because they follow a different law that they are not precipitated. This will appear more obviously hereafter, when we come to examine the constitution of the metallic salts.

3. When sulphur combines with a metal, the proportion remains unchanged, though the sulphur be converted into an acid, and the metal into an oxide. Thus the proportion of metal and sulphur in sulphate of copper is the same as in sulphuret of copper. Hence sulphuret of lead, when treated with nitric acid, is converted into neutral sulphate of lead, sulphuret of antimony into sulphate of antimony, and so on. This law, which is of great importance in practical chemistry, and very much facilitates the analysis of the metalline salts, was first pointed out by Berzelius.

4. The oxygen in a metallic protoxide is equal to half the sulphur in the sulphuret of the same metal, supposing the weight of the metal in both cases 100. This canon was first specified by Berzelius. It depends obviously upon the fact above established, that an atom of sulphur is twice the weight of an atom of oxygen, and holds only in those cases where the protoxide is a compound of one atom of metal and one atom of oxygen; and the sulphuret, of one atom of metal and one atom of sulphur. It may hold also when the oxide contains two atoms of oxygen, and the sulphuret two atoms of sulphur. This is the case with the black oxide of iron and magnetic pyrites. Hence the canon is of some utility, by enabling us the better to determine the constitution of the sulphurets; which, like the oxides, are susceptible of considerable variation.

5. In combinations of two bodies containing each a quantity of oxygen, the weight of oxygen in each body is either equal, or one contains twice, thrice, four times, &c. as far as eight times, the quantity of oxygen in the other. This law has been laid down by Berzelius;† but I must acknowledge I entertain considerable

* Mem. d'Arcueil, ii. 157.

† Ann. de Chim. lxxxiii. 119.

doubts about its accuracy. It will be better to leave the investigation of the subject till we come to examine the composition of the different salts, in all of which the two constituents contain oxygen. If it hold it will indicate a certain regularity in the relative weights of the atoms of bodies which I have not yet observed.

6. Water is capable of combining both with acids and bases. When it unites with an acid it acts the part of a base, and contains the same quantity of oxygen that the base would contain. Therefore the least quantity of water that can combine with sulphuric acid must contain 20 parts of oxygen. Hence the strongest possible sulphuric acid is a compound of

Acid	77 $\frac{1}{3}$
Water	22 $\frac{2}{3}$
	<hr/>
	100

When the water combines with a base, it acts the part of an acid, and combines in the same proportion. Hence such compounds are called *hydrates*. This canon has also been laid down by Berzelius. I must confess that I have not hitherto met with sufficient evidence of its accuracy to induce me to put much confidence in it; but we shall be able to judge better when we come to examine the constitution of the hydrates, than we can at present.

7. In combinations composed of more than two bodies containing oxygen, the oxygen of that constituent which contains the least of it is a common divisor of all the portions of oxygen found in the other bodies. This law, likewise laid down by Berzelius, evidently depends upon the kind of combination which these bases make with oxygen. If they are each combinations of one atom of base with one atom of oxygen, the quantity of oxygen present in all will be the same. If one is a protoxide, and another a deutoxide, then the one will contain double the quantity of oxygen in the other. And since oxygen always unites by atoms, it is obvious that all the quantities of oxygen will be divisible by one atom of oxygen. Hence the law.

If we were accurately acquainted with the constitution of the earths, this law would be of great importance to the mineralogist. It would enable him to distinguish between chemical combinations and mechanical mixtures. I have no doubt that it will ultimately throw a new light upon the chemical analysis of minerals; even at present it may be applied with some success, taking the imperfect knowledge that we have as a basis.

8. When two combustible bases unite they always combine in such a proportion that, when oxidized, either the quantity of

oxygen uniting with each would be the same, or the oxygen in the one would be twice, thrice, &c. that in the other. This is another law laid down by Berzelius, and obviously depends upon this fact, that the two bodies must either unite atom to atom, or a certain number of atoms of the one must combine with one atom of the other.

This law might be applied successfully to determine which of the metallic alloys are chemical combinations, and which are mechanical mixtures. For example, there can be no doubt that copper and zinc combine chemically. Now from the following table it will appear that the weight of an atom of these metals is as follows:—

Copper	8·000
Zinc	4·315

Therefore, if they unite atom to atom, brass ought to be a compound of 100 copper and 53·93 zinc. Now if any person will be at the trouble to analyse brass, he will find that this is very nearly the proportion of the ingredients.

In like manner bell-metal seems to be a compound of 5 atoms of copper to 1 atom of tin; and the metal for mirrors, of 4 atoms of copper and 1 atom of tin. If mercury unites atom to atom with tin, it ought to dissolve somewhat less than half its weight of that metal. And if the same law holds with zinc, it ought to dissolve about $\frac{1}{3}$ th of its weight of that metal.

III. *Relative Weight of the Atoms of different Substances determined from Chemical Analysis.*

Before we can draw up a table of the relative weights of the atoms of bodies, we must fix upon some one whose atom shall be represented by unity. Mr. Dalton has made choice of hydrogen for that purpose, because it is the lightest of all known bodies. Sir Humphry Davy has followed his example; but he has doubled the weight of an atom of oxygen, and consequently of all other bodies, by the arbitrary supposition that water is composed of two atoms of hydrogen and one of oxygen. Dr. Wollaston and Professor Berzelius have both proposed the atom of oxygen as the most convenient unit: nor can there be any hesitation in embracing their plan. Oxygen is in fact the substance by means of which the weight of the atoms of almost all other bodies is determined. It enters into a much greater number of combinations than any other known body; hence the great advantage attending a convenient number for that body to the practical chemist.

It would remove a great deal of confusion, which is at present very conspicuous in this department of the science, if chemists would agree to represent the weight of the atoms by

the same numbers. The following table is submitted to the chemical world as more convenient than the methods hitherto followed; and as the means employed in determining the numbers is every where stated, it were to be wished that they were adopted by chemists in general, as far as they are accurate. If the same numbers were steadily employed by all persons, they would soon be recollected by chemists, who would thus be able to state the composition of every compound without being obliged to refer to a book. The utility of such a recollection to the practical chemist is too obvious to be pointed out.

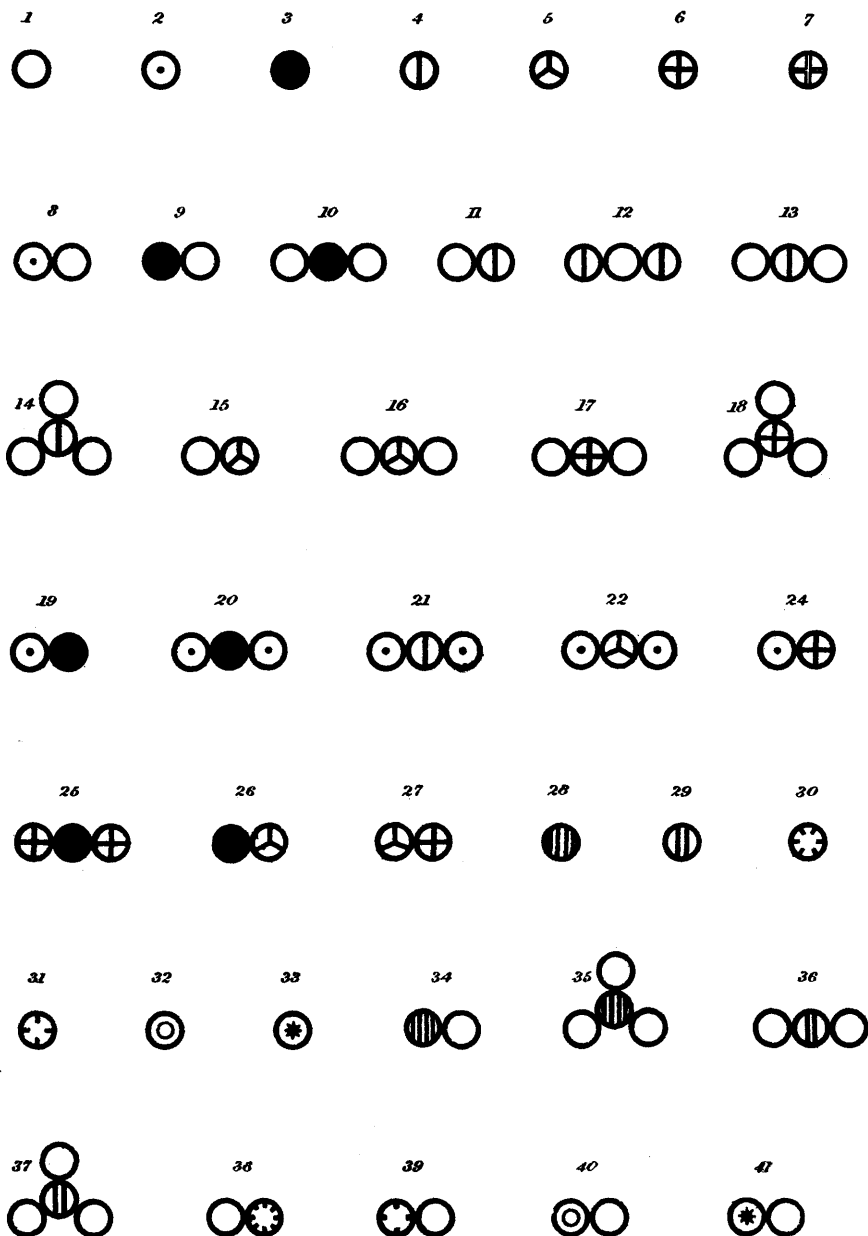
Weight of an atom.

1. Oxygen	1·000
2. Hydrogen	0·132
3. Carbon	0·751 ^a
4. Azote	0·878 ^b
5. Phosphorus	1·320 ^c

^a This is obtained from carbonic acid, which I conceive, with Dalton, to be a compound of 2 atoms of oxygen and 1 atom of carbon. When charcoal is burned in oxygen gas, the bulk of the gas is not altered, it is merely changed into carbonic acid. Hence if from the weight of 100 cubic inches of carbonic acid gas = 46·313 grains, we subtract the weight of 100 cubic inches of oxygen gas = 33·672 grains, the remainder = 12·641 grains gives us the weight of carbon in 100 cubic inches of carbonic acid gas. This shows us that carbonic acid is composed of 27·29 parts of carbon and 72·71 of oxygen. My analysis of olefiant gas gives 0·748 for the weight of an atom of carbon, which comes very near the preceding.

^b This number is obtained from nitrous gas, which, I think, Mr. Dalton has successfully shown to be a compound of 1 atom azote and 1 atom oxygen; and Gay-Lussac has proved it to be a compound of equal measures of azotic gas and oxygen gas. The number adopted by Sir H. Davy to represent an atom of azote when reduced to our proportions would be 0·860, and that of Mr. Dalton 0·714. Ammonia gives us a different ratio if we suppose it, with Dalton, to be a compound of 1 atom of hydrogen and 1 atom of azote. The weight of an atom of azote in that case would be 0·584; but if we consider ammonia as composed of 2 atoms of hydrogen and 1 atom of azote, then the weight of an atom of azote comes out 0·876. Hence I conceive ammonia to be a ternary compound.

^c This number is deduced from phosphoric acid. Sir H. Davy has ascertained that the quantity of oxygen in phosphoric acid is double of that in phosphorous acid. Hence, I think,



SYMBOLS OF CHEMICAL BODIES.

Engraved by J. Shury for D. Thomson's Annals. Published by R. Baldwin, Paternoster Row, July 1852.

		Weight of an atom.
6. Sulphur		2.000
7. Boron		
	Number of atoms.	Weight of a particle.
8. Water, composed of ...	1 o + 1 h	1.132 ^d
9. Carbonic oxide	1 o + 1 c	1.751 ^e
10. Carbonic acid	2 o + 1 c	2.751
11. Nitrous gas ^f	1 o + 1 a	1.878

it follows, that phosphoric acid is a compound of 1 atom of phosphorus and 2 atoms of oxygen. Farther, it has been ascertained that when phosphorus is burnt in oxygen gas each grain of phosphorus absorbs $4\frac{1}{3}$ cubic inches of oxygen. Therefore phosphoric acid is composed of 100 phosphorus and 151.52 of oxygen, and phosphorous acid of 100 phosphorus and 75.76 of oxygen: and an atom of oxygen is to an atom of phosphorus as 75.76 to 100, or as 1 to 1.320 nearly.

^d I conceive water to be a binary compound. The opinion advanced by Sir H. Davy, that it is a ternary compound of an atom of oxygen united to 2 atoms of hydrogen, cannot, I think, be supported.

^e It has been ascertained by accurate experiments that 100 measures of carbonic oxide for complete combustion require 50 measures of oxygen gas, and that the residue is 100 measures of carbonic acid gas. Hence it follows that the quantity of oxygen in carbonic acid is just double what exists in carbonic oxide, while the quantity of carbon in both is the same. Berthollet's objections to this conclusion are inadmissible. He seems, indeed, to have given up the point himself.

^f The determination of the compounds into which azote and oxygen enter is attended with considerable difficulty. The reason for considering nitrous gas as a binary compound, and its analysis, have been stated before. I consider it as exactly determined. The reasons assigned by Dalton for considering nitrous oxide as a compound of 2 atoms of azote and 1 atom of oxygen, seem to me conclusive: and Gay-Lussac has shown that it contains just twice as much azote as nitrous gas, supposing the oxygen in both the same. Hence its composition must be as stated in the table. The acid analysed by Cavendish and Davy, and called nitric acid, I conceive to have been in fact nitrous acid. What Mr. Dalton calls oxy-nitric acid is true colourless nitric acid, which seems only to exist in combination with water or a base.

V. *The Bakerian Lecture. On the elementary Particles of certain Crystals.* By William Hyde Wollaston, M. D. Sec. R. S.

Read November 26, 1812.

AMONG the known forms of crystallized bodies, there is no one common to a greater number of substances than the regular octohedron, and no one in which a corresponding difficulty has occurred with regard to determining which modification of its form is to be considered as primitive; since in all these substances the tetrahedron appears to have equal claim to be received as the original from which all their other modifications are to be derived.

The relations of these solids to each other is most distinctly exhibited to those who are not much conversant with crystallography, by assuming the tetrahedron as primitive, for this may immediately be converted into an octohedron by the removal of four smaller tetrahedrons from its solid angles. (Fig. 1.)

The substance which most readily admits of division by fracture into these forms is fluor spar; and there is no difficulty in obtaining a sufficient quantity for such experiments. But it is not, in fact, either the tetrahedron or the octohedron, which first presents itself as the apparent primitive form obtained by fracture.

If we form a plate of uniform thickness by two successive divisions of the spar, parallel to each other, we shall find the

H 2

plate divisible into prismatic rods, the section of which is a rhomb of $70^{\circ}32'$ and $109^{\circ}28'$ nearly; and if we again split these rods transversely, we shall obtain a number of regular acute rhomboids, all similar to each other, having their superficial angles 60° and 120° , and presenting an appearance of primitive molecule, from which all the other modifications of such crystals might very simply be derived. And we find, moreover, that the whole mass of fluor might be divided into, and conceived to consist of, these acute rhomboids alone, which may be put together so as to fit each other without any intervening vacuity.

But, since the solid thus obtained (as represented fig. 2.) may be again split by natural fractures at right angles to its axis (fig. 3.), so that a regular tetrahedron may be detached from each extremity, while the remaining portion assumes the form of a regular octohedron; and, since every rhomboid, that can be obtained, must admit of the same division into one octohedron and two tetrahedrons, the rhomboid can no longer be regarded as the primitive form; and since the parts into which it is divisible are dissimilar, we are left in doubt which of them is to have precedence as primitive.

In the examination of this question, whether we adopt the octohedron or the tetrahedron as the primitive form, since neither of them can fill space without leaving vacuities, there is a difficulty in conceiving any arrangement in which the particles will remain at rest: for, whether we suppose, with the Abbé HAÜY, that the particles are tetrahedral with octohedral cavities, or, on the contrary, octohedral particles regularly arranged with tetrahedral cavities, in each case the mutual contact of adjacent particles is only at their edges; and

although in such an arrangement it must be admitted that there may be an equilibrium, it is evidently unstable, and ill adapted to form the basis of any permanent crystal.

More than three years have now elapsed since a very simple explanation of this difficulty occurred to me. As in the course of that time I had not discovered it to be liable to any crystallographical objection, and as it had appeared satisfactory to various mathematical and philosophical friends to whom I proposed it, I had engaged to make this the subject of the Bakerian Lecture of the present year, hoping that some further speculations, connected with the same theory, might lead to more correct notions than are at present entertained of crystallization in general.

At the time when I made this engagement, I flattered myself that the conception might be deserving of attention from its novelty. But I have since found, that it is not altogether so new as I had then supposed it to be; for by the kindness of a friend, I have been referred to Dr. HOOKE's *Micrographia*, in which is contained, most clearly, one essential part of the same theory.

However, since the office of a lecturer is properly to diffuse knowledge already acquired, rather than to make known new discoveries in science, and since these hints of Dr. HOOKE have been totally overlooked, from having been thrown out at a time when crystallography, as a branch of science, was wholly unknown, and consequently not applied by him to the extent which they may now admit, I have no hesitation in treating the subject as I had before designed. And when I have so done, I shall quote the passage from Dr. HOOKE, to shew how exactly the views which I have taken have, to a certain extent,

corresponded with his; and I shall hope that, by the assistance of such authority, they may meet with a more favourable reception.

The theory to which I here allude is this, that, with respect to fluor spar and such other substances as assume the octohedral and tetrahedral forms, all difficulty is removed by supposing the elementary particles to be perfect spheres, which by mutual attraction have assumed that arrangement which brings them as near to each other as possible.

The relative position of any number of equal balls in the same plane, when gently pressed together, forming equilateral triangles with each other (as represented perspectively in fig. 4.) is familiar to every one; and it is evident that, if balls so placed were cemented together, and the stratum thus formed were afterwards broken, the straight lines in which they would be disposed to separate would form angles of 60° with each other.

If a single ball were placed any where at rest upon the preceding stratum, it is evident that it would be in contact with three of the lower balls (as in fig. 5.), and that the lines joining the centres of four balls so in contact, or the planes touching their surfaces, would include a regular tetrahedron, having all its sides equilateral triangles.

The construction of an octohedron, by means of spheres alone, is as simple as that of the tetrahedron. For if four balls be placed in contact on the same plane in form of a square, then a single ball resting upon them in the centre, being in contact with each pair of balls, will present a triangular face rising from each side of the square, and the whole together will represent the superior apex of an octohedron; so that a

sixth ball similarly placed underneath the square will complete the octohedral group, fig. 6.

There is one observation with regard to these forms that will appear paradoxical, namely, that a structure which in this case was begun upon a square foundation, is really intrinsically the same as that which is begun upon the triangular basis. But if we lay the octohedral group, which consists of six balls, on one of its triangular sides, and consequently with an opposite triangular face uppermost, the two groups, consisting of three balls each, are then situated precisely as they would be found in two adjacent strata of the triangular arrangement. Hence in this position we may readily convert the octohedron into a regular tetrahedron, by addition of four more balls. (fig. 7.) One placed on the top of the three that are uppermost forms the apex; and if the triangular base, on which it rests, be enlarged by addition of three more balls regularly disposed around it, the entire group of ten balls will then be found to represent a regular tetrahedron.

For the purpose of representing the acute rhomboid, two balls must be applied at opposite sides of the smallest octohedral group, as in fig. 9. And if a greater number of balls be placed together, fig. 10 and 11, in the same form, then a complete tetrahedral group may be removed from each extremity, leaving a central octohedron, as may be seen in fig. 11, which corresponds to fig. 3.

The passage of Dr. HOOKE, from which I shall quote so much as to connect the sense, is to be found at page 85 of his *Micrographia*.

“ From this I shall proceed to a second considerable phenomenon, which these diamants (meaning thereby quartz

“ crystals) exhibit, and that is the regularity of their figure
 “ ———This I take to proceed from the most simple principle
 “ that any kind of form can come from, next the globular ;
 “ for——I think I could make probable, that all these regular
 “ figures arise only from three or four several positions or
 “ postures of globular particles, and those the most plain and
 “ obvious, and necessary conjunctions of such figured particles
 “ that are possible——And this I have *ad oculum* demonstrated
 “ with a company of bullets, so that there was not any regu-
 “ lar figure which I have hitherto met withal of any of those
 “ bodies that I have above named, that I could not with the
 “ composition of bullets or globules imitate almost by shaking
 “ them together.

“ Thus, for instance, we find that globular bullets will of
 “ themselves, if put on an inclining plain so that they may
 “ run together, naturally run into a triangular order compos-
 “ ing all the variety of figures that can be imagined out of
 “ equilateral triangles, and such you will find upon trial all the
 “ surfaces of alum to be composed of——

“ —nor does it hold only in superficies, but in solidity also ;
 “ for it's obvious that a fourth globule laid upon the third in
 “ this texture composes a regular tetrahedron, which is a very
 “ usual figure of the crystals of alum. And there is no one
 “ figure into which alum is observed to be crystallized, but
 “ may by this texture of globules be imitated, and by no
 “ other.”

It does not appear in what manner this most ingenious philosopher thought of applying this doctrine to the formation of quartz crystal, of vitriol, of salt-petre, &c. which he names. This remains among the many hints which the peculiar jealousy

of his temper left unintelligible at the time they were written, and which, notwithstanding his indefatigable industry, were subsequently lost to the public, for want of being fully developed.

We have seen, that by due application of spheres to each other, all the most simple forms of one species of crystal will be produced, and it is needless to pursue any other modifications of the same form, which must result from a series of decrements produced according to known laws.

Since then the simplest arrangement of the most simple solid that can be imagined, affords so complete a solution of one of the most difficult questions in crystallography, we are naturally led to inquire what forms would probably occur from the union of other solids most nearly allied to the sphere. And it will appear that by the supposition of elementary particles that are spheroidical, we may frame conjectures as to the origin of other angular solids well known to crystallographers.

The obtuse Rhomboid.

If we suppose the axis of our elementary spheroid to be its shortest dimension, a class of solids will be formed which are numerous in crystallography. It has been remarked above, that by the natural grouping of spherical particles, fig. 10, one resulting solid is an acute rhomboid, similar to that of fig. 2, having certain determinate angles, and its greatest dimension in the direction of its axis. Now, if other particles having the same relative arrangement be supposed to have the form of oblate spheroids, the resulting solid, fig. 12, will still be a regular rhomboid; but the measures of its angles will be different from those of the former, and will be more

or less obtuse according to the degree of oblateness of the primitive spheroid.

It is at least possible that carbonate of lime and other substances, of which the forms are derived from regular rhomboids as their primitive form, may, in fact, consist of oblate spheroids as elementary particles.

It deserves to be remarked, that the conjecture to which we are thus led by a natural transition, from consideration of the most simple form of crystals, was long since entertained by HUYGHENS,* when treating of the oblique refraction of Iceland spar, which he so skilfully analysed. The peculiar law observable in the refraction of light by that crystal, he found might be explained on the supposition of spheroidical undulations propagated through the substance of the spar, and these he thought might perhaps be owing to a spheroidical form of its particles, to which the disposition to split into the rhomboidal form might also be ascribed.

By some oversight, however, the proportion of the axes of such an elementary spheroid is erroneously stated to be 1 to 8; but this is probably an error of the press, instead of 1 to 2,8, for I find the proportion to be nearly 1 to 2,87. In fig. 15, F is the apex of a tetrahedron cut from an acute rhomboid similar to fluor spar, and the sections of two spheres are represented round the centres F and C. I is the apex of a corresponding portion cut from the summit of a rhomboid of Iceland spar, as composed of spheroids having the same diameter as the spheres. In the former, the inclination FCT of the edge of the tetrahedron to its base is $54^{\circ} 44'$; in the latter, the inclination ICT is $26^{\circ} 15'$; and the altitudes FT, IT are as

* HUYGHENII Op. Reliq. Tom. I. Tract. de Lumine, p. 70.

the tangents of these angles 14.14 to $493 :: 2,87 : 1$, which also expresses the ratio of the axis of the sphere to that of the spheroid, or the proportional diameters of the generating ellipse.

Hexagonal Prisms.

If our elementary spheroid be on the contrary oblong, instead of oblate, it is evident that by mutual attraction, their centres will approach nearest to each other when their axes are parallel, and their shortest diameters in the same plane (fig. 13.) The manifest consequence of this structure would be, that a solid so formed would be liable to split into plates at right angles to the axes, and the plates would divide into prisms of three or six sides with all their angles equal, as occurs in phosphate of lime, beryl, &c.

It may further be observed, that the proportion of the height to the base of such a prism must depend on the ratio between the axes of the elementary spheroid.

The Cube.

Although I could not expect that the sole supposition of spherical or spheroidical particles would explain the origin of all the forms observable among the more complicated crystals, still the hypothesis would have appeared defective, if it did not include some view of the mode in which so simple a form as the cube may originate.

A cube may evidently be put together of spherical particles arranged four and four above each other, but we have already seen that this is not the form which simple spheres are naturally disposed to assume, and consequently this hypothesis

alone is not adequate to its explanation, as Dr. HOOKE had conceived.

Another obvious supposition is that the cube might be considered as a right angled rhomboid, resulting from the union of eight spheroids having a certain degree of oblateness (2 to 1) from which a rectangular form might be derived. But the cube so formed would not have the properties of the crystallographical cube. It is obvious, that, though all its diagonals would thus be equal, yet one axis parallel to that of the elementary spheroid would probably have properties different from the rest. The modifications of its crystalline form would probably not be alike in all directions as in the usual modifications of the cube, but would be liable to elongation in the direction of its original axis. And if such a crystal were electric, it would have but one pair of poles instead of having four pair, as in the crystals of boracite.

There is, however, an hypothesis which at least has simplicity to recommend it, and if it be not a just representation of the fact, it must be allowed to bear a happy resemblance to truth.

Let a mass of matter be supposed to consist of spherical particles all of the same size, but of two different kinds in equal numbers, represented by black and white balls; and let it be required that in their perfect intermixture every black ball shall be equally distant from all surrounding white balls, and that all adjacent balls of the same denomination shall also be equidistant from each other. I say then, that these conditions will be fulfilled, if the arrangement be cubical, and that the particles will be in equilibrio. Fig. 14 represents a cube so constituted of balls, alternately black and

white throughout. The four black balls are all in view. The distances of their centres being every way a superficial diagonal of the cube, they are equidistant, and their configuration represents a regular tetrahedron; and the same is the relative situation of the four white balls. The distances of dissimilar adjacent balls are likewise evidently equal; so that the conditions of their union are complete, as far as appears in the small group: and this is a correct representative of the entire mass, that would be composed of equal and similar cubes.

Since the crystalline form and electric qualities of boracite are perhaps unique, any explanation of properties so peculiar can hardly be expected. It may, however, be remarked, that a possible origin of its four pair of poles may be traced in the structure here represented; for it will be seen that a white ball and a black one are regularly opposed to each other at the extremities of each axis of the cube.

An hypothesis of uniform intermixture of particle with particle, accords so well with the most recent views of binary combination in chemistry, that there can be no necessity, on the present occasion, to enter into any defence of that doctrine, as applied to this subject. And though the existence of ultimate physical atoms absolutely indivisible may require demonstration, their existence is by no means necessary to any hypothesis here advanced, which requires merely mathematical points endued with powers of attraction and repulsion equally on all sides, so that their extent is *virtually* spherical, for from the union of such particles the same solids will result as from the combination of spheres impenetrably hard.

There remains one observation with regard to the spherical form of elementary particles, whether actual or virtual, that

must be regarded as favourable to the foregoing hypothesis, namely, that many of those substances, which we have most reason to think simple bodies, as among the class of metals, exhibit this further evidence of their simple nature, that they crystallize in the octohedral form, as they would do if their particles were spherical.

But it must, on the contrary, be acknowledged, that we can at present assign no reason why the same appearance of simplicity should take place in fluor spar, which is presumed to contain at least two elements; and it is evident that any attempts to trace a general correspondence between the crystallographical and supposed chemical elements of bodies must, in the present state of these sciences, be premature.

Note. A theory has lately been advanced* by M. PRECHTL, which attempts to account for various crystalline forms from the different degrees of compression that soft spheres may be supposed to undergo in assuming the solid state. It is supposed, that with a certain degree of softness and of relative attraction, the particles will be surrounded each by four others, and will all be tetrahedral, although in fact it be demonstrably impossible that tetrahedrons alone should fill any space.

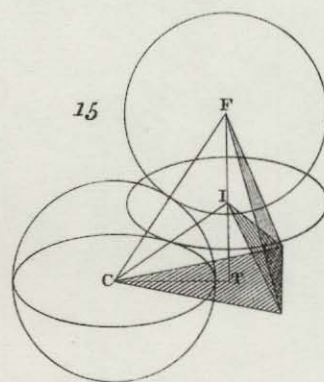
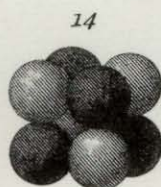
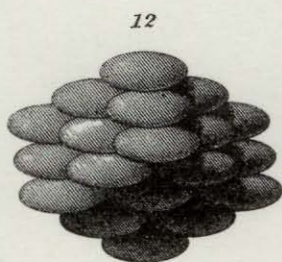
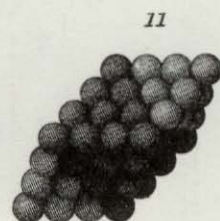
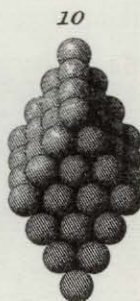
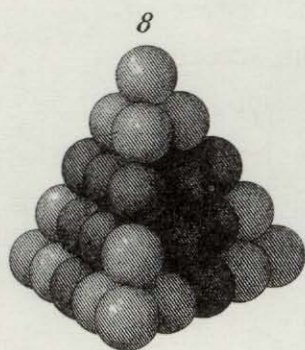
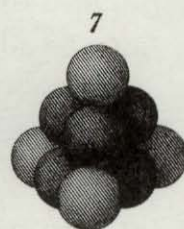
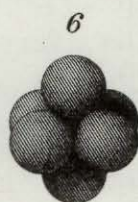
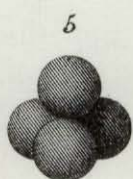
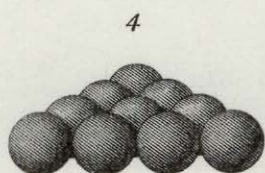
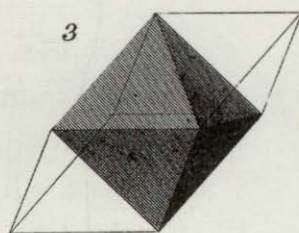
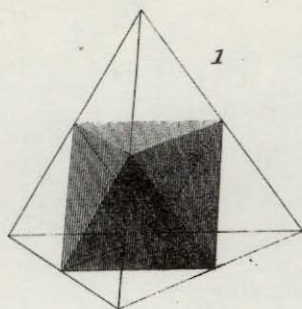
It is next supposed, that soft spheres less compressed will be surrounded by five others, and will be formed into triangular prisms, comprised under five similar and equal planes. That they should be similar is impossible, and it is further demonstrable, that when the triangular termination of such a

* Journal des Mines, No. 166.

prism is equal in area to each rectangular side of the prism, so as to present equal resistance, according to the hypothesis, then the triangular faces will be nearer to the centre in the proportion of three to four, so that the attractions will not be equal as the hypothesis would require.

A third hypothesis of M. PRECHTL is, that the degree of compressibility may be such that each particle will be surrounded by six others, giving it the form of a cube, which, it must be admitted, is a very possible supposition.

All further application of the same hypothesis is precluded by M. PRECHTL, by denying that one particle can be surrounded by more than six others; although in fact it is most evident, that any sphere when not compressed will be surrounded by twice that number, and consequently by a slight degree of compression will be converted into a dodecahedron, according to the most probable hypothesis of simple compression.



ARTICLE VII.

Essay on the Cause of Chemical Proportions, and on some Circumstances relating to them: together with a short and easy Method of Expressing them. By Jacob Berzelius, M.D. F.R.S. Professor of Chemistry at Stockholm.

I. *On the Relation between Berthollet's Theory of Affinities and the Laws of Chemical Proportions.*

SOME chemists have affirmed that the existence of chemical proportions is contrary to the principles of the theory of affinities with which the illustrious Berthollet has enriched chemistry. On that account they have refused to adopt it. But if, on the one hand, the knowledge of chemical proportions, which we at present possess, does not accord with all the applications made by Berthollet, and by other chemists, of his theory; on the other hand, it is incontestible, that these principles have never been refuted, but are more and more confirmed, the more they are examined. Chemists, before Berthollet, were misled by considering the weakest of the two chemical forces, or affinities, opposing each other as null. Berthollet pointed out that error, and showed the effect which the chemical mass produces.

Berthollet himself, far from denying the possibility of chemical proportions, has contributed a good deal to prove their existence, although the numbers resulting from his analytical experiments be not always very accurate. He has proved that when the elements cease to oppose each other, in consequence of their chemical mass, their combinations always take place in definite and invariable proportions. The doubts entertained by some chemists of the truth of Berthollet's principles originate certainly from the conduct of some of his zealous supporters, who have extended his doctrine to cases to which it does not apply, and have maintained the existence of indefinite combinations even when the action of the chemical mass cannot interfere. This opinion no doubt occasioned the fine experiments of Proust, whose object was to show that, when the metallic oxides absorb more oxygen, they pass at once from one degree of oxidation to another, without passing through the intermediate steps; and that what had been considered as an intermediate step was merely a mixture of a perfect oxide with an imperfect one.

The effects of the chemical mass are produced when, for example, three bodies, A, B, and C, exist together in the same solution; that is to say, in mutual contact; and when both A and B have an affinity for C, and endeavour to form the new combinations, A C and B C, which still remain in solution, and of course preserve their contact with the surplus of A and

B, which exists in the solution. If it has the strongest affinities, it combines with a greater proportion of C than B does: but though the attractions between A and C be greater than those between B and C, A is not able to draw to itself the whole of C, to the exclusion of B. In such a case, the portion of C combined with A to that combined with B will be determined by the strength of the affinity, and by the proportion of each present in the solution. Any person may satisfy himself of the reality of this division of C, by pouring concentrated muriatic acid into a solution of sulphate of copper. The solution, which was formerly blue, acquires a green colour by the addition of the muriatic acid (for muriate of copper is green); and this colour becomes stronger the more muriatic acid is added. The cause of this phenomenon is, that the affinity of the muriatic acid, though the weaker, still continues to act, and acts with more intensity the greater the quantity of that acid present. If, for example, 100 parts of sulphuric acid, and 100 parts of muriatic acid, divide 100 parts of oxide of copper between them, so that the sulphuric acid takes 80 parts and the muriatic 20 parts, it is clear that the force with which 100 of sulphuric acid remain in combination with 80 of oxide is equal to the force with which 100 muriatic acid remain in combination with 20 of oxide; that is to say, that the two opposite forces are in equilibrium. If any one of these combinations should separate from the solution—if the sulphate of copper, for example, should begin to crystallize; the phenomena would change. A new force, crystallization, would be added. This force does not act merely by abstracting a part of the chemical mass, but likewise as a positive force, capable of counterbalancing and of being counterbalanced.

It is obvious that in all this there is nothing inconsistent with the laws of chemical proportions. But it will be said that the 100 parts of sulphuric acid combined with the 80 parts of oxide of copper, and the 100 of muriatic acid with the 20, are not combined according to the laws of chemical proportions. It is obvious that the surplus of each of these acids is employed in counterbalancing the surplus of its antagonist, and cannot be considered as combined with the oxide of copper. Of consequence, the part of each acid really combined with the oxide is neutralized according to the laws of chemical proportions. I conceive that this single example is sufficient to show that the principles of Berthollet's theory are not inconsistent with the laws of chemical proportions.

II. *On the Cause of Chemical Proportions.*

The fact that bodies combine in definite proportions when other forces do not oppose their re-union, added to the observa-

tion that when two bodies, A and B, combine in different proportions, the additional portions of the one are always multiples by whole numbers, 1, 2, 3, 4, &c. lead us to conclude the existence of a cause in consequence of which all other combinations become impossible. Now *what is that cause?* It is obvious that the answer to this question must constitute the principal basis of chemical theory.

When we reflect on this cause it appears at first evident that it must be of a mechanical nature; and what presents itself as the most probable idea, and most conformable to our experience, is, that bodies are composed of atoms, or of molecules, which combine 1 with 1, 1 with 2, or 3, 4, &c.; and the laws of chemical proportions seem to result from this with such clearness and evidence, that it seems very singular that an idea so simple and so probable has not only not been adopted, but not even proposed before our own days. As far as I know, the English philosopher, Mr. John Dalton, guided by the experiments of Bergman, Richter, Wenzel, Berthollet, Proust, and others, was the first person who endeavoured to establish that hypothesis. Sir H. Davy has lately assured us that Mr. Higgins, in a book published in 1789, established the same hypothesis. I have not seen the work of Mr. Higgins, and can only notice the circumstance on the authority of Davy.*

Notwithstanding the great clearness and simplicity which characterize this hypothesis, it is connected with great difficulties, which make their appearance when we apply it to a number of chemical phenomena. These difficulties naturally excite doubts as to the truth of the hypothesis. Among the numerous experiments which I have made in order to discover the chemical proportions in which bodies unite, I have met with cases when, notwithstanding the completest agreement with the laws which I conceived myself to have discovered, the composition of a body could not be explained according to the hypothesis which we are

* The work of Higgins on *Phlogiston* is certainly possessed of much merit, and anticipated some of the most striking subsequent discoveries. But, when he wrote, metallic oxides were so little known, and so few exact analyses existed, that it was not possible to be acquainted with the grand fact that oxygen, &c. always unite in determinate proportions which are multiples of the minimum proportion. The atomic theory was taught by Bergman, Cullen, Black, &c., just as far as it was by Higgins. The latter, indeed, states some striking facts respecting the gases, and anticipated Gay-Lussac's theory of volumes; but Mr. Dalton first generalized the doctrine, and thought of determining the weight of the atoms of bodies. He showed me his table of symbols, and the weights of the atoms of six or eight bodies, in 1804; and I believe the same year explained the subject in London in a course of lectures delivered in the Royal Institution. The subject could scarcely have been broached sooner. But about the same time several other persons had been struck with the numbers in my table of metallic oxides published in my *Chemistry*; and the doctrine would have certainly been started by others if Dalton had missed it. --T.

considering. I shall state some of these cases, without, however, considering them as absolute proofs against the hypothesis, but rather as difficulties which we must endeavour to surmount, in order to obtain a clear and well established theory of chemical proportions.

I shall begin with a short explanation of the corpuscular theory, such as I conceive it. I shall employ the word *atoms* to signify the corpuscles, or smallest parts of which bodies are composed. When I say the *smallest parts*, I mean that they cannot be divided into other parts still smaller. I do not enter into any discussion whether matter be infinitely divisible or not, but take it for granted that an atom is mechanically indivisible; and of course that a fraction of an atom cannot exist. I suppose likewise that atoms are all spherical, and that they have all the same size. (This last circumstance is not necessarily attached to the idea of atoms, but it is absolutely necessary if regular figures are to result from their union, and if they unite in definite proportions, even in the most complicated combinations). It appears likewise necessary that when an atom of the body, A, combines with one or more atoms of the body B, to form a new compound atom, the atom of A touches each of the atoms of B. Hence a compound atom is formed by the juxtaposition of several elementary atoms; just as an *aggregate* is formed by the juxtaposition of different homogeneous atoms. But the difference consists in this, that in the first case an electric discharge takes place of the specific polarity of the heterogeneous atoms, which cannot take place between homogeneous atoms. (See my conjectures on this subject in Nicholson's Journal for March 1813, p. 154.)

A compound atom, for very obvious reasons, cannot be considered as spherical; but as it is composed of atoms mechanically indivisible, or which cannot be separated by mechanical means, the compound atom is justly as completely mechanically indivisible as the elementary atom. It is likewise evident that an atom composed of $A + 3 B$ ought to be greater, and to have a different figure from an atom composed of $A + B$. The former ought to have the form of a triangular and equilateral pyramid, while the latter must have a linear form.

We may divide the atoms into two classes: 1. Elementary atoms: 2. Compound atoms. The compound atoms are of three different species; namely, 1. Atoms formed of two elementary substances united. We shall call them *compound atoms of the first order*. 2. Atoms composed of more than two elementary substances: and as these are only found in organic bodies, or bodies obtained by the destruction of such organic matter, we shall call them *organic atoms*. 3. Atoms formed by the union of two or more compound atoms, as, for example, the *salts*. We shall call them *compound atoms of the second order*.

The greatest number of spherical atoms of the same diameter, capable of touching a single atom of the same diameter, is 12. Hence it follows that $A + 12 B$ contains the greatest number of atoms which a *compound atom of the first order* can contain. If, on the other hand, we pay attention to the electric polarity of the atoms, an atom of A cannot combine with more than 9 atoms of B, if the atom $A + 9 B$ preserve any part of the electric polarity originally belonging to A: for example, *oxymuriatic acid*, which is a compound of 1 atom of muriatic radicle and 8 atoms of oxygen, still preserves a part of the original polarity of the radicle, by means of which it re-acts; while the *supersulphuret of arsenic*, of which I shall give an account in the sequel, and which is composed of 1 atom of arsenic and 12 atoms of sulphur, has no other electrochemical re-action than that of sulphur.

It is contrary to sound logic to represent a single compound atom of the first order as composed of 2 or more atoms of A combined with 2 or more atoms of B; as, for example, $2 A + 2 B$, $2 A + 3 B$, $7 A + 7 B$, &c.: for in such a case there is no obstacle, either mechanical or chemical, to prevent such an atom from being divided, by means purely mechanical, into 2 or more atoms of more simple composition. Besides, such a composition would almost totally destroy chemical proportions. Hence it follows, that in stating the result of an analysis conformably to the views of the corpuscular theory, we must always consider one of the constituents as unity, that is to say, as a single atom. What I have stated here appears to me to be necessary consequences, or reflections inseparable from the theory of atoms, not one of which can be rejected without committing what is called *contradictio in adjecto*.

I shall now give an account of the difficulties to which I conceive the corpuscular theory is liable.

1. The first of these difficulties is, the circumstance that there are combustible bodies, *iron*, for example, which unite only with two doses of oxygen, the second of which is only $1\frac{1}{2}$ times greater than the first. This difficulty, however, is only apparent: for I have already, in my former memoirs on this subject, shown that, in all probability, it is owing to our being still unacquainted with all the degrees of oxidation of which the body in question is capable. The multiple $1\frac{1}{2}$ implies the existence of an inferior degree of oxidation to that which we consider as the minimum. I hope in this essay to prove the truth of this opinion in a still more satisfactory manner.

2. I think I have proved that when two oxides combine they always unite in such proportions that each contains either an equal quantity of oxygen, or the one contains a quantity which is a multiple by a whole number of the oxygen in the other.

This law, though in itself conformable to the corpuscular theory, admits, on the one side, of combinations inconsistent with that theory; and, on the other hand, it excludes combinations perfectly conformable with that theory. I shall explain this by an example. Let O be oxygen, A and B two combustible bodies. The law which we are considering admits of a combination of $A + 3 O$ with $1\frac{1}{2} B O$, because $1\frac{1}{2} \times 2 = 3$; and we shall see immediately that such combinations exist, though, according to the corpuscular theory, they appear absurd. On the other hand, the law does not admit the combination of $A + 3 O$ with $B + 2 O$, though such a combination be conformable to the theory of atoms. The black oxide of copper is composed, according to our present knowledge, of 1 atom of metal and 2 atoms of oxygen, and sulphuric acid of 1 atom of sulphur and 3 atoms of oxygen. We know that there is a subsulphate of copper in which the acid and the oxide contain each equal quantities of oxygen. Of course, this subsulphate must contain for every atom of sulphuric acid an atom and a half of oxide of copper. It is true that we may object to this, that there is some appearance that sulphuric acid is composed of 6 atoms of oxygen to 1 of sulphur. But I shall have occasion to discuss this opinion when I come to speak particularly of sulphur. Arsenic acid, from new experiments of which I shall give an account in the sequel, is composed of 1 atom of arsenic and 6 atoms of oxygen. The yellow oxide of lead is composed of 1 atom of metal and 2 atoms of oxygen. The arseniate of lead is composed in such a manner that the acid contains three times as much oxygen as the oxide, that is to say, of an atom of acid and an atom of oxide. The subarsenate of lead is composed in such a manner that the acid contains twice as much oxygen as the oxide; that is to say, of an atom of acid and an atom and a half of oxide.

If we suppose that the yellow oxide of lead contains but one atom of oxygen, this subsalt ceases to be an objection to the atomic theory; but in that case we meet with an equally formidable objection in the composition of the red oxide of lead.

I have endeavoured to prove that two different oxides of the same radicle sometimes combine in such a manner that each contains an equal quantity of oxygen, or that the one contains two, three, &c. times as much as the other. Among these combinations there are some which do not agree with the hypothesis of atoms: for example, the red oxide of iron contains 3 volumes of oxygen, and the black oxide 2 volumes. Gay-Lussac has lately found that the oxide of iron formed at a high temperature by the action of the vapour of water is composed of 100 iron + 37.8 oxygen. But this combination of the two oxides is composed in such a manner that the red oxide in the compound contains exactly twice as much oxygen as the black: that is to

say, that it is composed of $1\frac{1}{3}$ atom of the first and 1 atom of the second. One method of refuting this objection would be to consider the black oxide of iron as containing 4 atoms of oxygen, the red as containing 6, and the intermediate oxide as containing 5: but in this case the analysis of Gay-Lussac is incorrect. He should have obtained 36.8 of oxygen instead of 37.8. But we are not at present acquainted with any example of a body containing 5 atoms of oxygen; and I shall prove in the sequel that the oxide in question cannot be considered as a particular oxide, since it possesses all the characters of a compound of the red and black oxides of iron.

3. We have seen that an elementary atom cannot combine with more than 12 elementary atoms. Inorganic nature has not yet presented us with any body which is inconsistent with this supposition: but among organic bodies such examples are very frequent. It is in the study of the composition of organic bodies that our knowledge of the laws of chemical proportions, and of the electrochemical theory, will one day reach that degree of perfection which the human mind is capable of giving it. I shall give the composition of oxalic acid as an example of the constitution of an organic atom. I analysed this acid by decomposing it, by distilling oxalate of lead mixed with a quantity of brown oxide of lead, and making the gaseous products pass through muriate of lime, and then through limewater. I repeated this analysis with so little variation, that I consider my results as a close approximation to the truth. In neither of these analyses did I obtain as much water as amounted to a quantity of hydrogen equivalent to 1 per cent. of the acid: but we cannot conceive an atom of oxygen to be united with a fraction of an atom of hydrogen. We must therefore consider the small quantity of hydrogen which we obtain as an entire atom. If we admit water to be a compound of 2 atoms of hydrogen and 1 atom of oxygen, and carbonic acid of 1 atom of carbon and 2 atoms of oxygen, it follows from my analysis, that the atom of oxalic acid is composed of 1 atom of hydrogen, 27 atoms of carbon, and 18 atoms of oxygen; that is to say, that it consists of an atom of hydrogen combined with 45 other atoms.

If, on the other hand, we chuse to consider the organic atoms as consisting of an atom of compound radicle combined with 1 or more atoms of oxygen, and of course oxalic acid as composed of an atom of radicle and 3 atoms of oxygen: the radicle in that case will be a compound of 1 atom hydrogen + 27 atoms carbon, and will remain equally inapplicable to the hypothesis of atoms. It follows, likewise, that an atom of oxalic acid is eleven times greater than an atom of sulphuric acid, and fifteen times greater than an atom of potash: yet in the superoxalate of

potash discovered by Dr. Wollaston an atom of potash should be combined with $1\frac{1}{2}$ atom of oxalic acid.

I own that I do not know how these observations, and several others which it would be superfluous to mention here, can be reconciled with the hypothesis of atoms: but it would be rash to conclude that we shall not be able hereafter to explain these apparent anomalies in a satisfactory manner. Till that time comes, the hypothesis of atoms can neither be adopted nor considered as true.

I have already, in preceding memoirs, made mention of another method of viewing chemical proportions—a method founded on a fact discovered by Gay-Lussac; namely, that bodies when in the state of gases unite either in equal volumes, or 1 volume of one combines with 2, 3, &c. volumes of the other. This fact has been already verified by several distinguished chemists. From what we know respecting definite proportions, it follows, that it would hold with all bodies in the temperature and pressure at which they would assume the gaseous form. Hence there is no other difference between the theory of atoms and that of volumes, than that the one represents bodies in a solid form, the other in a gaseous form. It is clear, that what in the one theory is called an *atom*, is in the other theory a *volume*. In the present state of our knowledge the theory of volumes has the advantage of being founded upon a well constituted fact, while the other has only a supposition for its foundation. In the theory of volumes we can figure to ourselves a demi-volume, while in the theory of atoms a *demi-atom* is an absurdity. On the other hand, the theory of volumes has a disadvantage from which the atomic theory is free; namely, the existence of compound bodies, especially of an organic nature, which we cannot suppose ever to have existed in the form of gas.

I ought to observe, that we have here, as well as in the theory of atoms, *elementary volumes* and *compound volumes of the first and second order*. It follows from the laws of chemical proportions, that two compound volumes, containing a common constituent, ought to combine in such a manner that they contain either equal volumes of this common constituent, or that the one contains two, three, &c. times the number of volumes of the other. It is almost demonstrated that an elementary volume never combines with $1\frac{1}{2}$ volume of another elementary substance: but at present we are obliged to admit that this sometimes happens with compound volumes.

In the theory of volumes we cannot suppose the combination of 2 volumes with 3, &c.: for on such a supposition there can be no reason assigned why 4 volumes should not combine with 5, 7 with 9, 999 with 1000, &c.: so that in such a case no reason

could be assigned for the existence of chemical proportions. Here, as well as in the theory of atoms, it is absolutely necessary that in each compound one of the constituents should be considered as a single volume.

It is evident that if the weight of the volumes of the elementary bodies be known, and expressed in numbers, we have nothing more to do in every case of analysis but to count the relative number of volumes of the constituent parts, whatever the form of their aggregation may be : but in order to obtain the relative weights of the elementary volumes expressed in numbers, that is to say, to obtain their specific gravity in the form of gas, we must have a general measure with which we may compare them. We may chuse among the elementary bodies one, the weight of a volume of which must be denoted by unity; just as water has been chosen for unity in determining the specific gravity of liquids and solids.

There are only two elementary bodies possessed of the requisite qualities to serve as our unit. These are *oxygen* and *hydrogen*. But hydrogen has disadvantages from which oxygen is free. The weight of a volume of hydrogen is so small, that if we employ it as our unit, the number representing a volume of some of the metals becomes inconveniently great. Besides, hydrogen enters much less frequently into compounds than oxygen; and of course the number 100, when applied to hydrogen, does not nearly so much facilitate calculation as when it is applied to oxygen. Add that oxygen constitutes among elementary bodies a particular class, and, as it were, the centre round which chemistry turns. It exists in the greater number of unorganic bodies, and without exception in all the products of organic nature. I think, then, that it is at once most convenient, and most agreeable to the scientific views of chemistry, to take oxygen as our unit. I shall represent its volume by the number 100.

The question which we have now to resolve is this, *What is the specific gravity of all other elementary bodies in the form of gas, compared with that of oxygen?* This question is not easily answered : for at present there are no other bodies except oxygen and hydrogen which we are capable of weighing in the state of gas. All other bodies are converted into gas at such high temperatures that it is not in our power to ascertain their weight. We must therefore endeavour to discover the weight of their volumes by other means. Our results will be, doubtless, very uncertain; but not altogether unsuccessful; as I hope to be able to show in the sequel.

In the first place, it appears reasonable to suppose that bodies ought to combine most generally in equal volumes : but in examining the greatest number of the combinations of elementary

bodies, we find that those which are distinguished by a strong affinity between their constituent parts, and by the force of their chemical affinity for other bodies, contain evidently more than one volume of one of their elements. This is the case with water, carbonic acid, nitrous gas, &c., and, with very few exceptions, it is always the electro-negative element the volume of which is multiplied. On the other hand, in bodies composed distinctly of equal volumes, such as the nitric suboxide (*azote*), and carbonic suboxide (*carbonic oxide*), we find all the negative properties which characterize the suboxides. This leads me to suppose that all the suboxides are composed of equal volumes of their elements. It follows from these observations that the most part of the salifiable oxides and acids ought to be composed of more than one volume of oxygen for each volume of radicle.

Experiment seems to prove that if a combustible radicle combine in preference with 2 or 3 volumes of oxygen, it combines likewise in preference with 2 or 3 volumes of sulphur. If a salifiable oxide be composed of 1 volume of radicle and 2 or 3 volumes of oxygen; and if we neutralize this oxide by any acid whatever, it is to be supposed that the neutral combination which results ought to contain for 1 volume of the radicle of the oxide as many volumes of the radicle of the acid as the oxide contains volumes of oxygen; and, consequently, that the number of times which the acid contains the oxygen of the oxide will be the number of volumes of oxygen combined with 1 volume of the radicle of the acid: for example, we consider sulphuric acid as composed of 1 volume of radicle and 3 volumes of oxygen; because it is very probable that the quantity of sulphur and of oxygen capable of combining at an elevated temperature with a given portion of lead constitute equal volumes. But if we want to know by another method how many volumes of oxygen exist in sulphuric acid, we have only to examine the composition of some sulphate; for example, sulphate of iron (*sulphas ferrosus*). The black oxide of iron contains 1 volume of metal and 2 volumes of oxygen. It follows, from what has been said, that the black oxide of iron ought to be neutralized by a quantity of acid containing 2 volumes of sulphur for every volume of iron: so that the number of volumes of the sulphur of the acid and of the oxygen of the oxide shall be equal. But the acid contains three times as much oxygen as the base; consequently, it is composed of 3 volumes of oxygen and 1 volume of sulphur. If, instead of the sulphate of iron, we were to make choice of the persulphate of iron (*sulphas ferricus*), it is evident that in such a case the iron is combined with 3 volumes of sulphur, so that the result is just the same.

This observation would be sufficient to determine the volume of a substance whose oxide possesses the characters of an acid, or

of an electro-negative body, were it not for the numerous exceptions which exist to the rule, some very remarkable instances of which I shall have occasion to notice in the sequel. Hence it is always necessary, in order to discover those exceptions, and to verify the weight of the volume sought to compare the result of the preceding calculation with the known degrees of oxidation of the substance whose volume is wanted. If, for example, we find that an acid or electro-negative oxide is neutralized by a quantity of base or electro-positive oxide which contains $\frac{1}{3}$ of the oxygen in the acid, this acid will appear to contain 3 volumes of oxygen. But if among the oxides of the radicle of this acid we find one which contains half the oxygen of the acid, it is clear that the saline combination in question is an exception, and that the acid must contain 6 instead of 3 volumes of oxygen. I refer, for a farther explanation of this, to what I shall say in the sequel concerning *arsenic* and *chromium*.

The preceding observations explain why, when a salifiable base has combined with more oxygen, it requires always an additional volume of acid for every volume of oxygen which it has absorbed. It is for the same reason that oxygen appears to determine exclusively the composition of bodies; though there can be no doubt that every element contributes equally to that composition.

While treating in the sequel of each particular substance, I shall explain the way in which I determine the weight of a volume of it, and likewise state the experiments on which the calculation is founded. As none of our experiments, except from accident, can be perfectly correct, and as a small error in the result often increases in the calculation, it is not possible that my determinations can be perfectly exact: but I hope to approach within very near limits, at least, of the truth. The difference in the analytical results will point out to us the limits of error, and show us degrees beyond which our determinations cannot be incorrect. I shall give an account of these minima and maxima indicated by experiment, as well as of the experiments themselves, which point them out. We have, for example, every reason to believe that a volume of sulphur weighs 201: but some experiments raise it as high as 210, while others sink it as low as 200. As we cannot determine at present which of these numbers is most exact, it is good to know within what limits our knowledge is uncertain.

As far as I know, the English chemists Dalton, Davy, and Young, are the only persons who have yet attempted to make these determinations; and they have proceeded in a manner somewhat different. Mr. Dalton, to whom the honour of the first attempt is due, has endeavoured to determine the relative

weights both of simple and compound atoms. (*New System of Chemical Philosophy*.) Davy, though he has not adopted the atomic theory of Dalton, has embraced the doctrine of definite proportions; and what Dalton calls an *atom*, he calls a *proportion*. (*Elements of Chemical Philosophy*.) Dr. Young, in his *Introduction to Medical Literature*, has made similar determinations; but what Davy calls *proportion*, Young calls *combining weight*. But none of these philosophers have attempted to give any great degree of exactness to their determinations. They have frequently even omitted stating the experiments from which these determinations are derived. The method which they have adopted of giving round numbers, though it facilitates the recollection and calculation, is scarcely consistent with the object of scientific researches, and ought to be rejected: for even supposing that perfect exactness could never be obtained, it is nevertheless the object towards which all our efforts should be directed.

(To be continued.)

ARTICLE V.

Essay on the Cause of Chemical Proportions, and on some Circumstances relating to them: together with a short and easy Method of expressing them. By Jacob Berzelius, M.D. F.R.S. Professor of Chemistry at Stockholm.

(Continued from Vol. II. p. 454.)

III. *On the Chemical Signs, and the Method of employing them to express Chemical Proportions.*

WHEN we endeavour to express chemical proportions, we find the necessity of chemical signs. Chemistry has always possessed them, though hitherto they have been of very little utility. They owed their origin, no doubt, to the mysterious relation supposed by the alchemists to exist between the metals and the planets, and to the desire which they had of expressing themselves in a manner incomprehensible to the public. The fellow-labourers in the anti-phlogistic revolution published new signs founded on a reasonable principle, the object of which was, that the signs, like the new names, should be definitions of the composition of the substances, and that they should be more easily written than the names of the substances themselves. But, though we must acknowledge that these signs were very well contrived, and very ingenious, they were of no use; because it is easier to write an abbreviated word than to draw a figure, which has but little analogy with letters, and which, to be legible, must be made of a larger size than our ordinary writing. In proposing new chemical signs, I shall endeavour to avoid the inconveniences which rendered the old ones of little utility. I must observe here that the object of the new signs is not that, like the old ones, they should be employed to label vessels in the laboratory: they are destined solely to facilitate the expression of chemical proportions, and to enable us to indicate, without long periphrases, the relative number of volumes of the different constituents contained in each compound body. By determining the weight of the elementary volumes, these figures will enable us to express the numeric result of an analysis as simply, and in a manner as easily remembered, as the algebraic formulas in mechanical philosophy.

The chemical signs ought to be letters, for the greater facility of writing, and not to disfigure a printed book. Though this last circumstance may not appear of any great importance, it ought to be avoided whenever it can be done. I shall take, therefore, for the chemical sign, the *initial letter of the Latin name of each elementary substance*: but as several have the same initial letter, I shall distinguish them in the following manner:—1. In the class which I call *metalloids*, I shall employ the initial letter only, even when this letter is common to the metalloid and to some metal. 2. In

the class of metals, I shall distinguish those that have the same initials with another metal, or a metalloid, by writing the first two letters of the word. 3. If the first two letters be common to two metals, I shall, in that case, add to the initial letter the first consonant which they have not in common: for example, S = sulphur, Si = silicium, St = stibium (antimony), Sn = stannum (tin), C = carbonicum, Co = cobaltum (cobalt), Cu = cuprum (copper), O = oxygen, Os = osmium, &c.

The chemical sign expresses always one volume of the substance. When it is necessary to indicate several volumes, it is done by adding the number of volumes: for example, the *oxidum cuprosum* (protoxide of copper) is composed of a volume of oxygen and a volume of metal; therefore its sign is $\text{Cu} + \text{O}$. The *oxidum cupricum* (peroxide of copper) is composed of 1 volume of metal and 2 volumes of oxygen; therefore its sign is $\text{Cu} + 2 \text{O}$. In like manner, the sign for sulphuric acid is $\text{S} + 3 \text{O}$; for carbonic acid, $\text{C} + 2 \text{O}$; for water, $2 \text{H} + \text{O}$, &c.

When we express a compound volume of the first order, we throw away the +, and place the number of volumes above the letter: for example, $\text{Cu} \overset{3}{\text{O}} + \text{S} \overset{3}{\text{O}} =$ sulphate of copper, $\text{Cu} \overset{2}{\text{O}} + 2 \text{S} \overset{3}{\text{O}} =$ persulphate of copper. These formulas have this advantage, that if we take away the oxygen we see at once the ratio between the combustible radicles. As to the volumes of the second order, it is but rarely of any advantage to express them by formulas as one volume; but if we wish to express them in that way, we may do it by using the parenthesis, as is done in algebraic formulas: for example, alum is composed of 3 volumes of sulphate of alumina and 1 volume of sulphate of potash. Its symbol is $3 (\text{Al} \overset{2}{\text{O}} + 2 \text{S} \overset{3}{\text{O}}) + (\text{Po} + 2 \text{S} \overset{3}{\text{O}})$. As to the organic volumes, it is at present very uncertain how far figures can be successfully employed to express their composition. We shall have occasion only in the following pages to express the volume of ammonia. It is $6 \text{H} + \text{N} + \text{O}$, or $\overset{6}{\text{H}} \text{N} \text{O}$.

IV. Weight of elementary Volumes compared with that of Oxygen Gas.

A.—Oxygen.

The volume of oxygen is expressed by the letter O. It is considered = 100.

B.—The Metalloids.

1. *Sulphuricum, sulphur* (S).—I have already mentioned that we may determine the volume of this body by the quantity of sulphur which combines with a given weight of metal compared with the oxygen which combines with the same metal. It is to be supposed that the relative quantities of sulphur and oxygen have the same

ARTICLE III.

Remarks on the Essay of Dr. Berzelius on the Cause of Chemical Proportions. By John Dalton.

(Read before the Manchester Society, Dec. 24, 1813.)

It may perhaps seem premature to animadvert on an essay before the whole of it has been published ; but as Dr. Berzelius has stated certain objections to the atomic theory of chemistry in that part of his essay published in the *Annals of Philosophy* for this month, which, if left unanswered, may be thought by some to present insuperable difficulties, I have judged it expedient to make a few remarks on the subject immediately, by way of obviating. Engaged as I have been for some years past, and still continue to be, in a labyrinth of chemical investigation, it may well be imagined I cannot find much time for controversy ; yet the scruples of one who has so eminently distinguished himself as a fellow labourer in the same field of science, and whose views and opinions in a great measure approximate to my own, are certainly entitled to consideration. Whatever our theoretical speculations may be, they are of little avail unless supported by facts ; and, notwithstanding the modern improvements in the practice of chemistry, no theory of it can advance far without meeting with the difficulties which too often arise from inaccurate observation. I hope to prove to the satisfaction of Dr. Berzelius that some of the difficulties he finds in pursuing the atomic theory are of this kind, and that the rest are only imaginary.

The first division of Dr. Berzelius' essay, on the relation between Berthollet's theory of affinities and the laws of chemical proportion, contains an admirable exposition of those facts which Berthollet brought forward in so conspicuous a point of view in his chemical theory, and which his zealous followers have magnified in a still greater degree. A better explanation could, I think, be scarcely given in fewer words.

In the second division on the cause of chemical proportions, Dr. Berzelius, after ascribing to me the principal share in announcing and developing the corpuscular or atomic theory, proceeds to give an explanation of what *he* conceives it to be. His ideas on this head are somewhat at variance with mine ; and this is one point on which I wish to be clearly understood, and shall endeavour in what follows to enable the reader to discriminate betwixt us.

Dr. B. seems to hold it necessary that all atoms should be of *the same size*. This, he thinks, is required in order to form bodies into regular figures. Now this is no part of my doctrine. I do maintain that all the atoms of any homogeneous body, A, are of the same *size* as well as weight ; and that all the atoms of B are of the same *size* and weight ; but I see no sufficient reason for concluding that the atoms of A are of the same *size* as those of B. The probability

is rather, I think, that the atoms are of *unequal sizes*; and the size may be in direct proportion to the weight, or otherwise. There can, in fact, be only three suppositions on all this subject:— 1. That the sizes are all the same. 2. That the sizes are as the weights. 3. That the sizes are unequal, but not as the weights. My system is not restricted to any of these suppositions; but if any one can show that the regular organization of bodies is inconsistent with one or other of these suppositions, it must, of course, be rejected. Till that is done, one is about as plausible as another.

It is rather amusing to me to observe the different manners in which a cursory view of the atomic system strikes different persons. Dr. Thomson was the first who, from some hints I gave him, published an outline of the system in the third edition of his chemistry. He used the phrase *density of the atoms* indifferently for *weight of the atoms*, thereby implying that all atoms are of the *same size*, and differ only in *density*; but he has since very properly discontinued the use of the phrase. This also appears to be the notion of Berzelius. On the other hand, Dr. Bostock seems to think (see Nich. Jour. vol. xxviii. p. 292) that the *sizes* of atoms must be in direct proportion to their *weights*.

Dr. Berzelius thinks it necessary that when an atom of A combines with an atom of B, it must touch it. We shall agree in this mode of expressing the fact; but our ideas may differ materially with regard to the signification. The contiguous atoms of all elastic fluids touch each other by means of thin atmospheres of heat: I neither know nor admit of any other sort of contact. The solid impenetrable matter, if there be such, constitutes the centre of the atom, never comes into contact with that of any other, as far as is known; because it appears to be impossible to deprive bodies of their heat. The atoms of bodies may, therefore, co-exist at various distances; in the solid and liquid forms they are comparatively near, and in the elastic form distant; but in all the forms they are subject to variation, in this respect, from temperature and pressure. It is probable that the atoms of oxygen gas might be condensed into a volume, so that their distance should not exceed that of oxygen and hydrogen in an atom of steam, and yet not unite chemically so as to change their form. Hence it should seem that the notion of particles *touching* each other is not a sufficient criterion of chemical union. In elastic fluids chemical union is best conceived, I think, from the circumstance of two or more atoms of A and B uniting so as to form a common centre of repulsion.

With regard to the *figure* of atoms, Dr. Berzelius observes, that a compound atom cannot be considered as spherical, but that an elementary atom may be taken as such. Here, again, we should understand one another, whether *solid corpuscle* is meant, or *solid corpuscle united to an atmosphere of heat*, when we speak of an atom. If the former, then it is clear that compound atoms cannot be spherical; nor do I see any reason sufficient for supposing all simple atoms to be so; those of hydrogen may be spherical,

perhaps; those of oxygen may be regular tetrahedrons; those of azote may be cylinders of equal diameter and altitude; &c. &c. But if we understand atom in the latter sense, then not only the elementary atoms, but most of the compound atoms, are probably spherical, spheroidal, or some figure approaching to that of a sphere. Of all compound atoms, that consisting of 3 elementary atoms is probably most remote from a sphere; but when the compound one contains 5 or more simple ones, the figure must, I should suppose, be virtually a sphere.

What Dr. B. says of the *electric polarity* of atoms (vol. ii. p. 447) makes no necessary part of the atomic theory such as I maintain. Neither does the conclusion that 2 atoms of A cannot combine with 2 of B, 2 of A with 3 of B, &c. Such combinations, I apprehend, rarely exist; but I see no reason, either from theory or experience, for rejecting them. It may be said that such compound atoms are capable of division: true. But the parts may instantly unite again by virtue of an affinity; and hence they cannot, perhaps, be exhibited in a divided state. Olefiant gas, for instance, is known to consist of carbon and hydrogen united in the ratio of 1 atom to 1: but there is nothing that I know of to prevent their uniting 2 atoms of carbon to 2 of hydrogen, and the 4 atoms to be placed in the form of a rhombus, those of hydrogen being at the extremities of the longest diameter. Nitrous acid, too, may be adduced as an instance of 2 atoms of azote and 3 of oxygen. And even nitric acid seems most frequently to be found in composition as if constituted of 2 atoms of azote and 4 of oxygen united to 1 of base. However unlikely this may be, I see no absurdity in supposing that if 2 atoms of nitric acid, such as I have delineated in my Chemistry, were contiguous, they might coalesce by affinity, and refuse to take a third atom or compound of the like kind. Hence I disclaim the axiom that every compound atom must have a single atom for its nucleus or centre.

So much for the differences in our conceptions of the principles of the atomic theory. We come next to the difficulties to which Dr. Berzelius apprehends it is liable.

“The first of these difficulties is the circumstance that there are combustible bodies, *iron*, for example, which unite only with two doses of oxygen, the second of which is only $1\frac{1}{2}$ times greater than the first.” Here I perfectly agree with Dr. Berzelius, both as to the existence of the difficulty, and as to the solution of it which he has given. When the oxygen in the (supposed) protoxide of any metal is to that in the deutoxide as 1 to $1\frac{1}{2}$, that is, as 2 to 3, it is to be presumed that the real first oxide is not known, and that those two which are known are the second and third oxides. But this is not the only solution which such cases admit of, as will appear presently. My ideas on the oxides of iron were settled from some experiments I made in 1807, compared with the experiments of others then published. I concluded that 100 iron combine with 28 oxygen by solution in sulphuric acid, forming what is called the

black oxide; and with 42 oxygen by heat, &c. forming the red oxide. Hence 50 iron combine with 14 oxygen and with 21, and the combination of 50 iron with 7 oxygen to form the protoxide is unknown. It was in conformity with this reasoning that I published in the second part of my Chemistry, in 1810, the atom of iron to weigh 50. The details were not given, because I was not then describing the oxides. The facts are not at all at variance with the atomic theory; but it appears a strange circumstance that the first oxide cannot, by any means we are yet acquainted with, be obtained, whilst the second and third are readily. The circumstance, however, is not without parallels. We well know that sulphur takes 2 portions of oxygen to form sulphurous acid, and 3 to form sulphuric; but we scarcely recognise a compound of sulphur with 1 portion of oxygen. Again, carbonic acid gas has been known time immemorial; but carbonic oxide gas has been known only about twelve years: yet it is pretty evident that the latter is, theoretically, the more simple combination of the two.

The second difficulty which Dr. Berzelius states is so obscurely expressed that it requires an acute atomist to perceive the force of it. This may, perhaps, be partly owing to the translation, and to an error of the press, which last, however, is pretty readily corrected. He has discovered a law (which, for the sake of argument, I shall take for granted to be true,) "that when two oxides combine they always unite in such proportions that each contains either an equal quantity of oxygen, or the one contains a quantity which is a multiple by a whole number of the oxygen in the other." This law, though in itself conformable to the corpuscular theory, admits, (he says) on the one side, of combinations inconsistent with that theory; and, on the other side, it excludes combinations perfectly conformable with that theory. To illustrate these positions, he gives several examples: I shall take the first two. Let O be oxygen, A and B two combustible bodies; then $A + 3 O$ may combine with $B + 1\frac{1}{2} O$, because $1\frac{1}{2} \times 2 = 3$; and (he asserts) that such combinations exist, though according to the corpuscular theory they appear absurd. Now I think it must be obvious that this *second* difficulty is the same as the first, and admits of the same explanation which Berzelius has given; namely, that the body, B, in such case has in reality 3 atoms of oxygen for 1 of metal, the quantity of which oxygen we chuse to express by $1\frac{1}{2}$. And the union in question is 1 atom of the third oxide of B with 2 atoms of the third oxide of A, a combination perfectly consistent with the atomic theory, as well as with the law and the example just exhibited to view. The other example is, that the law does not admit $A + 3 O$ to unite with $B + 2 O$, though such combination be conformable to the theory of atoms. In reply to this, I may observe, that it is not the peculiar business of the atomic theory to explain why $A + 3 O$ do not unite with $B + 2 O$, any more than to show why all the metallic oxides do not mutually combine with each other; for it may be said there

is nothing apparent in the atomic theory to prevent such combinations.

After having the atomic principles in contemplation for ten years, I find myself still at a loss, occasionally, to discriminate between the combinations which contain 2 atoms of a given body from those which contain only 1 atom. Hence an atom that weighs 50 may be sometimes put down as weighing 100. It is owing to the difficulty on this head, I apprehend, that Berzelius considers the atom of lead at twice the weight I do; in consequence, he makes the yellow oxide of lead to consist of 1 metal and 2 oxygen. As for the red oxide of lead, I consider it, after Proust, as being probably made up of the yellow and brown oxides in combination.

One example adduced as incompatible with the atomic theory appears to me peculiarly unfortunate. It is an oxide of iron containing 37.8 oxygen upon 100 iron, discovered by Gay-Lussac. Now this may be accounted to be a compound of 2 atoms of the red oxide and 1 of the black; for such a compound must contain 37.3 oxygen upon 100 of iron, which agrees more nearly with the experiment than we have any right to expect in such case.

The third and last difficulty which Dr. Berzelius has brought forward as militating against the atomic theory is derived from the analysis of what he calls *organic atoms*; that is, atoms composed of more than two elementary substances. The atom of oxalic acid is adduced as an instance.

It would be a singularly curious circumstance, and well worth recording in the annals of chemistry, if the composition of the oxalic acid itself should bid defiance to the atomic theory, or to that of definite proportions, whilst the compounds formed with it were originally produced by Dr. Wollaston and Berard as exhibiting the most striking illustration of the doctrine. I was indeed surprised to see the results of such an analysis of oxalic acid published by Berzelius, to whose accuracy in general I can subscribe; but still more so to have it afterwards referred to as militating against my doctrine. He concludes its constitution must be 1 atom of hydrogen, 27 of carbon, and 18 of oxygen; that is, 1 atom of hydrogen with 45 other atoms. Were it a matter of necessity, an atomist might conceive 1 atom of hydrogen surrounded by 9 of carbon, and the compound globule to have 18 atoms of carbonic oxide adhering to it. But this would be an atom truly formidable, in every sense of the word, as the least friction must be supposed capable of producing a violent explosion of such a mass of elasticity. I cannot, however, doubt that Dr. Berzelius, having resumed the consideration, will very soon discover and acknowledge that his analysis is incorrect. In the mean time, I shall give my reasons for believing it to be so.

Dr. B. informs us in the *Ann. de Chim.* (tom. 81, p. 300) that 10 grains of oxalate of lead yielded by heat 7.42 of yellow oxide. Hence he infers the constitution of oxalate of lead to be 25.2 acid

and 74·8 oxide per cent. It is from the analysis of this compound that he derives his knowledge of the elements of the acid. My analysis of oxalate of lead, recently repeated, gives me 29 acid and 71 yellow oxide. Here then, in the offset, is a very material difference betwixt us as to facts: any chemist, however, is competent to satisfy himself on this head without appealing to authorities. Let a solution of acetate of lead be treated with oxalic acid, or any soluble oxalate, and the oxalate of lead will be immediately thrown down. Let it be carefully washed, dried, pulverized, and again dried in a temperature of 100°. If, then, 137 parts of this be put into a platina or iron spoon, and be very gradually heated to a low red to prevent loss by decrepitation, there will remain 97 parts of pure yellow oxide; giving the constitution of the oxalate as under; namely,

Lead	90
Oxygen	7
Oxalic acid	40
	<hr/>
	137

The quantity 137 is here preferred because the numbers thence resulting represent those for the respective atoms upon my system. According to the analysis of Berzelius, an atom of oxalic acid would weigh only 32·7, which is less than that of sulphuric acid; in fact, he finds $26\frac{1}{3}$ sulphuric acid in sulphate of lead, and only 25·2 of oxalic acid in the oxalate. Now it happens that all the modern chemists who have analysed the oxalates (Berzelius excepted) agree with me in making the oxalic acid heavier than the sulphuric, as may be seen from their analyses of the oxalate of lime below:—

	Lime.	Oxalic Acid.
Dr. Thomson	24	40
Gay-Lussac	24	38
Berard	24	32

N.B. The atom for sulphuric acid is 34 on this scale.

About two years ago I made a series of experiments on oxalic acid and the oxalates. I then determined (as I conceived) the constitution of the acid, assisted very materially by the masterly analysis of Gay-Lussac, with which I found my results very nearly accord, as well as by that of Dr. Thomson. The atom of oxalic acid, I apprehend, is constituted of 1 hydrogen and 2 carbonic acid; or of 1 hydrogen, 2 carbon, and 4 oxygen; the total weight being 39·8, or 40. This being reduced to 100, and compared with the modern analyses, the results will stand as under. Oxalic acid is composed of

	Per Theory.	Gay-Lussac.	Thomson.	Berzelius.
Hydrogen ..	2·5	2·75	4	·7
Carbon	27·1	26·56	32	35·0
Oxygen	70·4	70·69	64	64·3
	<hr/>	<hr/>	<hr/>	<hr/>
	100	100	100	100
		M 2		

The crystallized oxalic acid consists of 1 atom of acid and 2 of water. The proportions are as under :—

	Per Theory.	Thomson.	Berard.	Berzelius.
Real oxalic acid ..	71·4	77	72·7	71·25
Water	28·6	23	27·3	28·75
	<hr/> 100	<hr/> 100	<hr/> 100	<hr/> 100

It is remarkable that Berzelius determines the water in the crystals of oxalic acid, as it should seem, with great accuracy; but that when the acid is combined with lead it loses (according to him) about 14 per cent. *more* of water. Now this does not happen in the case of the other insoluble oxalates, such as that of lime; for Dr. Thomson found 77 parts out of 100 of crystallized oxalic acid to exist in the dry oxalate of lime obtained from it. This circumstance is of itself sufficient to render Berzelius' analysis of the oxalate of lead doubtful. Query: What temperature was his oxalate of lead dried in?

With respect to the *theory of volumes*, to which Berzelius seems inclined to give the preference rather than to that of atoms, it is not my intention to say much at present. I shall wait to see it more fully developed. I own I do not see how we are to remove the difficulties attending the atomic theory by substituting the term *volume* for that of atom; nor how "we can figure to ourselves a *demi-volume*, while in the theory of atoms a *demi-atom* is an absurdity." Notwithstanding this, whatever may come from the pen of Berzelius on the subject will, no doubt, be worthy the attention of the chemical world.

ARTICLE X.

An Address to those Chemists who wish to examine the Laws of Chemical Proportions, and the Theory of Chemistry in general.
By Jacob Berzelius, M. D. F.R.S. Professor of Chemistry in Stockholm.

MR. DALTON has published in the *Annals of Philosophy*, vol. iii. p. 174, Observations concerning my memoir On the Cause of Chemical Proportions. It has given me pain to think that the respectable Dalton has taken my ideas on the corpuscular theory as a criticism on his, between which he has pointed out the difference. I think I have expressed myself in that memoir with sufficient precision to make the reader sensible that I neither meant to give the opinions of Dalton, nor a correction of them. There is a very essential difference between the researches of Mr. Dalton and myself. Mr. Dalton has chosen the method of an inventor, by setting out from a first principle, from which he endeavours to deduce the experimental results. For my own part, I have been obliged to take the road of an ordinary man, collecting together a number of experiments, from which I have endeavoured to draw conclusions more and more general. I have endeavoured to mount from experiment towards the first principle; while Mr. Dalton descends from that principle to experiment. It is certainly a great homage to the speculations of Dalton if we meet each other on the road.

Among the numerous experiments which I have myself made relative to this subject, there are some which do not appear to agree

* I have reason to conclude, from observations which I made this summer, that the country between the Lomonds on the south, and Stonehaven on the north, including the Ochils, and the hills in the neighbourhood of Perth, Dundee, Red-head, and Montrose, is composed of rocks belonging to the old red sand-stone. Upon the southern extremity of these rocks the great coal-field of the Forth rests, and occupies the situation of a newer deposition.

with the atomic theory so well as the rest; and which of course I have not been able to explain in a satisfactory manner. There are others whose existence is not a necessary consequence of the atomic theory of Mr. Dalton. These, in my opinion, prove that there is still something wanting in that theory, and which must be added to it in order to render it more complete. In my memoir *On the Cause of Chemical Proportions* I have endeavoured to draw the attention of the reader to these difficulties. Mr. Dalton has endeavoured to remove them, but with a levity which I did not expect from him, and which appears to me injurious to the science. He begins with pointing out the reasons why he cannot be of my opinion respecting the relative size and form of the atoms, &c. I must observe that at the bottom of every speculation in the exact sciences there always remains something which cannot be verified by experiment, and on which, of course, the imagination is at full liberty to indulge. The reveries of one man may be more ingenious, more interesting, and more probable, than those of another; but the science never gains any thing by disputes about subjects which are not susceptible of proof. I shall therefore pass over that part of the question in silence.

Mr. Dalton states that the electro-chemical polarity of the atoms makes no necessary part of the atomic theory, such as he maintains; nor did I ever mean to convey any such idea to the reader. For my own part, in considering a corpuscular theory of chemistry, I conceived that it should constitute the fundamental theory of the science; and instead of being occupied with a part of the phenomena, ought to embrace the whole. But when we treat of atoms in a chemical theory, we ought to endeavour to find out the cause of the affinity of these atoms. We ought to endeavour to combine researches respecting the cause why atoms combine with researches into the cause why they combine only in certain proportions. I do not consider the conjectures which I hazarded on the electro-chemical polarity of the atoms as of much importance. I scarcely consider them in any other light than as an ideal speculation deriving some little probability from what we know of the chemical effects of electricity. Yet the ideas on the relation of atoms to their electro-chemical properties, ought in my opinion to constitute an essential part of the corpuscular theory of chemistry, such as I view it; because I consider it as the duty of a man of science to endeavour to reach the first principle of the science, even though it should be actually impossible to attain it.

Mr. Dalton disapproves the idea which I announced, that we ought not to suppose an atom composed of $2A + 2B$, $2A + 3B$, &c. He thinks that such combinations take place, though but seldom. He inclines even to the idea that olefiant gas may be composed of two atoms of carbon to two of hydrogen, placed in the form of a rhombus, those of hydrogen being at the extremities of the longest diameter. Is there a chemical fact which countenances such an idea of the construction of the atoms of olefiant

gas? If there be, the notion may be considered as an interesting conjecture; but if there be no such fact, the notion is a mere dream. There can be no doubt that if we give free liberty to our imagination in this manner, the science will degenerate into a mass of vain speculations, of no utility whatever, because founded on nothing but imagination. My idea, that in every inorganic combination one of the elements enters as unity, is founded on the circumstance that in all the inorganic bodies which I have analyzed, and I have analyzed a great number, I have found it to be so. Besides, if this were not the case, it is evident that all traces of chemical proportions would disappear in combinations which consist of various oxides, and could only be perceived in the most simple combinations, I have then founded my opinion on experience. Can Mr. Dalton produce an instance in which this opinion is obviously inaccurate?

Mr. Dalton then proceeds to remove the difficulties which I found attached to the corpuscular theory. I shall pass by the first, which he finds that I myself have obviated in a manner conformable to his opinion. The second difficulty consists in this—I have found compounds which are represented, for example, by $A O^3 + 1\frac{1}{2} B O$, which is contrary to the views of the atomic theory; while a combination of $A O^3 + B O^2$ does not exist, although it be conformable to that theory. Mr. Dalton removes the first part of these difficulties, by saying, “the body B in such a case has in reality three atoms of oxygen for one of metal, and the union in question is $2 A O^3 + B O^3$.” I have given two examples of which Mr. Dalton has said nothing. These examples are the subarseniate of lead ($As O^6 + 1\frac{1}{2} P O^2$), and the subsulphate of copper ($S O^3 + 1\frac{1}{2} Cu O^2$). It is evident that neither of these examples admits the explanation by which Mr. Dalton has endeavoured to remove the difficulty; for neither the oxide of lead nor copper can contain three atoms of oxygen. Mr. Dalton adds merely, that he considers with Proust, minium as a compound of yellow oxide and brown oxide of lead; from which it seems to follow that he considers the subarseniate of lead as $As O^6 + 3 P O$. But what reason has Mr. Dalton to consider minium as composed in this manner? The necessity of it for his theory? But this necessity proves nothing as long as the theory itself is sub judice, which it probably will be for a long time to come. We may likewise explain the subsulphate of copper by supposing sulphuric acid composed of $S + 6 O$, or black oxide of copper $Cu + O$, and of course the protoxide $2 Cu + O$. But here lies the difficulty; for we have other reasons for considering the acid as $S + 3 O$, and the oxide $Cu + 2 O$. These difficulties cannot be removed by a stroke of the pen. Yet I am persuaded that both myself and Mr. Dalton will in time make use of these very difficulties to determine the true number of atoms in such and such compound bodies; but we must in the first place make a much greater number of experiments on these subjects than we possess at present; for it is not speculation alone, but experi-

ment guided and accompanied by speculation, that can give us new information. Let me be allowed here to give an example. Hydrate of iron is so composed that the oxygen of the oxide is twice that of the water; but both Mr. Dalton and myself give to this oxide three atoms of oxygen. This hydrate, then, is $\text{Fe O}^3 + 1\frac{1}{2} \text{H}^2\text{O}$. I should certainly be disposed to explain this at once, by supposing that the oxide of iron contains six atoms of oxygen. But in order to see whether there be other proofs for such an idea, let us run over the combinations of the oxide of iron with other bodies. Let us examine, for example, the combinations of this oxide with acids which contain six atoms of oxygen, but which in their neutral saline combinations contain only three times as much oxygen as the base. If in these neutral combinations with these acids, the red oxide of iron does not constitute an exception to the general law, it ought likewise to contain six atoms of oxygen; for otherwise in the arseniate or chromate of iron there would be for each atom of iron half an atom of arsenic or chromium. Let us extend these researches still farther, and examine if the arseniates, chromates, &c. can be formed with oxides in which there is evidently no more than three atoms of oxygen, &c. The ultimate result of our researches will probably be that four and six atoms of oxygen, instead of three, are much more general than we have hitherto supposed; and that not only oxide of iron, but silica and various other oxides contain in fact six atoms of oxygen instead of three. I suppose that Mr. Dalton will agree with me that by such researches we may render much more complete the beautiful theory for which he feels himself so much interested, and for which we are in a great measure indebted to him.

I have considered it as a great difficulty attached to the atomic theory that it does not explain the laws concerning the combinations of the oxides with each other, namely, why the oxygen in the one is always a multiple by a whole number of that in the other. Mr. Dalton removes this difficulty by saying, "It is not the peculiar business of the atomic theory to explain it any more than to show why all the metallic oxides do not mutually combine with each other." But we must recollect that the principal circumstance in favour of the atomic theory is, that it gives a mechanical and very satisfactory cause why elementary atoms unite only in proportions which are multiples of each other. We have observed likewise that the compound atoms, that is to say, most of those which contain oxygen, combine likewise in a *multiplex ratio*, provided we attend only to the oxygen which they contain. It is clear that this must be owing to a cause similar to that which occasions similar proportions between elementary atoms; but the atomic theory throws no light on the subject. This must be admitted as something still wanting in the theory; for when a theory only explains one half of the phenomena which result from the principle which regulates these phenomena, it is surely incomplete. I differ, then, from Mr. Dalton, and must continue to consider the atomic theory

as imperfect, and as clogged with difficulties, till it give us satisfactory explanations of all the phenomena relative to the chemical proportions. I do not think that we are very far from this explanation, but this is not the place to dilate upon the subject.

Mr. Dalton continues to observe, that the difficulty presented by the new oxide of iron of Gay-Lussac has been employed by me in a manner "particularly unfortunate." Had not Mr. Dalton thought it of importance to the science to express his opinion of the first pages of my memoir, before he was acquainted with its general tenour and termination, he might have seen how I myself removed the difficulty in question, both in the memoir itself, and by my analysis of the magnetic iron ores, where I have shown that the numbers given by Gay-Lussac are inaccurate. (Försäk til et System for Mineralogien. Stockholm, 1814. p. 97.)* As to the expression which Mr. Dalton has employed, "particularly unfortunate," I should have been glad to be deceived respecting it, by too little knowledge of the exact meaning of the phrase.

Mr. Dalton finishes his observations by endeavouring to remove the difficulties which the composition of organic bodies presents, in which the number of elementary atoms is often very great. I had instanced the atom of oxalic acid as an example of the composition of organic bodies. The method employed by Mr. Dalton to remove that difficulty deserves attention. "Were it," says he, "a matter of necessity, an anatomist might conceive one atom of hydrogen surrounded by nine of carbon, and the compound globule to have 18 of carbonic oxide adhering to it. But this would be an atom truly formidable in every sense of the word, as the least friction must be supposed capable of producing a violent explosion of such a mass of elasticity. I cannot, however, doubt that Dr. Berzelius having resumed the consideration, will very soon discover and acknowledge that his analysis is incorrect. In the mean time, I shall give my reasons for believing it to be so."

The tone of confidence with which Mr. Dalton finds me in the wrong in this passage has surprised me a little, and so much the more, that "any chemist is competent to satisfy himself on this head without appealing to authorities." As to the organic atoms, and the difficulties which they present, it would be too long to discuss them here. I therefore refer the reader to a set of experiments on the subject, which I am at present publishing in the *Annals of Philosophy*. As to my experiments on oxalic acid and oxalate of lead, I acknowledge that on repeating them I have found slight inaccuracies; but none of these have been in favour of Mr. Dalton's opinion. I have found that the oxalate of lead had given me rather too little oxide of lead, and oxalic acid rather too much hydrogen. Mr. Dalton has candidly stated his manner of analyzing the oxalate in question, and the result which he obtained. I shall likewise state mine. I

* An English translation of this interesting work has been published, to which the reader is referred. T.

prepared oxalate of lead by pouring a solution of pure oxalic acid into a solution of pure and neutral nitrate of lead. I did not employ acetate of lead, because that salt combines in part with all the substances which precipitate from it, as I have shown in my experiments on carbonate of lead, and more particularly in my Essay on Organic Combinations. Oxalate of lead contains no water of combination; hence it is easily dried, and requires only to be heated a few degrees above the temperature of the atmosphere. I burnt it in a capsule of thin glass, of which I had exactly determined the weight. I heated it in the flame of a spirit lamp, taking care to apply the first heat near the edge of the glass, and advancing gradually to the centre. The oxalate takes fire and burns quietly. When the whole is burnt I allow it to cool. I now weigh the glass with the oxide which it contains. This oxide is mixed with a small quantity of metallic lead, reduced by the charcoal of the acid. I dissolve it in distilled vinegar, wash the residual lead, dry it, and weigh it. To the weight of the oxide found, I add the quantity of oxygen requisite to convert the metallic lead into oxide. By this method of experimenting, oxalate of lead gave me 75.46 per cent. of oxide of lead. I would not recommend to the reader to repeat this experiment in metallic vessels, as of platinum or iron. When platinum vessels are used, I find that nine times out of ten the reduced lead unites with the platinum and spoils it. As to iron, every body knows that it increases in weight in the fire. As to the water which I found in effloresced oxalic acid, and to the difference between the result of the analyses of oxalate of lime, and of my analysis of oxalate of lead, Mr. Dalton will give me leave to refer him to the experiments of those, who in their analysis of oxalate of lime, have not neglected the water of combination contained in that salt.

When I endeavoured to draw the attention of chemists to the difficulties in the atomic theory, it was not my intention to refute that hypothesis. I wanted to lay open all the difficulties of that hypothesis, that nothing might escape our attention calculated to throw light on the subject. I wished the experiments to verify the theory; and I should have considered it as absurd, if I had taken the opposite road. I placed beside the corpuscular theory, a theory of volumes; because that theory is in some measure connected with facts which may be verified. To those who think that the theory of volumes may be fatal to the corpuscular theory, I would observe, that both are absolutely the same thing; but that the theory of volumes has this immediate advantage over the other, that it may be more easily verified. Let us suppose for a moment, that the theory of volumes were absolutely demonstrated. We would then ask, what is the difference between a solid and a gaseous body? The answer would restore to the corpuscular theory its rights. It would be demonstrated by that of volumes. The only difference between the two theories consists in the words *atom* and *volume*, that is to say, in the state of aggregation of the elements.

Chemical proportions begin to be more generally studied; but chemists are not agreed about the laws which regulate them. One party waits the opinion of those whom they consider as authorities; and these last appear to suspend their judgment, because the opinion requires to be verified by experiments, the number and difficulty of which is revolting to their minds. Let me be permitted to point out here, what in my opinion ought to be the principal object of their examination.

Chemical proportions depend upon two cardinal points: 1. The proportions in which the elementary atoms unite. 2. The proportions in which the compound atoms combine. The first of these is a necessary consequence of the atomic theory; and as the number of combinations which it includes is very limited, almost the whole of them have been examined, without finding a single exception to the law. Hence this point is very generally admitted. The case is very different with the second point. It includes an almost infinite number of compounds, varying in their elements as to the number of compound atoms which they contain. I have examined a great number of these substances, and as they are for the most part composed of oxides, I paid particular attention to the oxygen which they contain. The laws which I considered myself as entitled to establish from these experiments are well known.

The first cardinal point being established we must endeavour to establish or refute the second. If the accuracy of my experiments be admitted, I think their number is such that the second point also may be considered as verified. If this accuracy be not admitted, it is obviously necessary to repeat my experiments, and produce other analogous ones. My experiments have informed me how very difficult and even painful this kind of labour is; but it is absolutely necessary. I know of only two chemists who have hitherto occupied themselves with this examination, namely, Mr. Vogel, of Bayreuth; and Dr. Thomson, of London. The first undertook the analysis of a set of double salts, mostly containing water of crystallization; that is to say, composed of three or four oxides. The results which he obtained corresponded with the law. Dr. Thomson has in a theoretic dissertation gone over a great number of saline combinations. He inclines to admit the law.

This law is of much more importance than may be supposed at first. It deserves therefore the most careful and impartial examination. Were it not for this law, no combination composed of several oxides could be calculated, nor any analysis verified in a decisive manner for the theory. For it is clear, that if there be combinations expressible, for example, by $2 A O^s + 4 B O^s + 7 C O + 5 H O$; or if nature were to allow us to change the numbers in the formulas in any manner whatever, in such a case, all idea of determinate proportions would disappear, in proportion as these combinations became more complicated.

It is likewise by means of the law concerning the combination

of oxides with each other, that we can hope to penetrate into the secrets of organic composition. When that law is demonstrated, the theory of chemical proportions may be considered as established.

It is absolutely necessary, that every person who repeats an analysis in order to ascertain its accuracy, should be acquainted with all the requisites to make an exact analysis, in the same degree as the author of the work which he proposes to examine. Otherwise, he takes upon him to judge his master. Accurate chemical analysis is half an art, half a science. He who does not unite both in one, will never be in a condition to make an exact analysis. We must always chuse that method in which the precision of result depends the least on the dexterity of the operator. We must likewise be able, from long experience, to avoid all the circumstances by which the result would be rendered inaccurate, that neither from forgetfulness, carelessness, or ignorance, we may neglect to observe and remove them. These circumstances are generally of such a nature that chemists usually pay no attention to them; yet they are of considerable importance when our object is to obtain the utmost possible accuracy. The most skilful chemist will continue long an apprentice in the art of analysis, if he has not been in the habit, from the commencement of his studies, to attend to these circumstances. Long experience is even often necessary before we discover their existence, unless we have the advantage of being informed by others.

When we have to judge between two different analytical methods, or between two different chemists, we must be well acquainted with the methods employed; and both the method and the reputation of the author ought to enter for something in our judgment. If, for example, we have to compare two experiments on the composition of a metallic oxide, one of which was made by dissolving the metal in nitric acid in a phial, from which the acid was then evaporated, and the residue exposed to a strong heat: if the other was made by precipitating the solution in nitric acid by means of an alkali, filtrating, &c., it is presumable, that supposing the same dexterity in the operators, the first experiment is more accurate than the second, because it has been less exposed to the influence of circumstances. It is necessary, however, that he who judges of two results, should know the circumstances that may render the one or the other inexact. We must know, for example, that the first experiment can scarcely have any other error, than giving too great a quantity of oxygen to the oxide. This may be either owing to the application of too little heat, or (which is more usual) to the glass not having resisted the action of the nitric acid during the evaporation, so that a little nitre is formed, the acid of which increases the weight of the oxygen that we think we have found. (This circumstance long deceived me in my first experiments before I perceived it.) The other method of operating can have no other error than indicating too little oxygen, if ammonia has been em-

ployed to precipitate the oxide. But if a fixed alkali has been employed, the result may be too great, as well as too small; for if the precipitate has not been well washed, there will remain in it nitrate of potash or of soda. Or if too much alkali has been employed in precipitating, a portion of that alkali for the most part combines with the oxide, and cannot afterwards be removed by washing. But I should never have done, were I to point out here all the circumstances requisite to make an accurate analysis, and to judge of its accuracy.

It is obvious, that the theory of chemical proportions is intimately connected with the general theory of chemistry; but it is necessary, that those who labour either to examine it, to verify it, to extend, or apply it, should have their eyes constantly fixed upon the whole of chemistry. They must not adopt any theoretical explanation, till they have seen that it is not in contradiction with any other part of the theory, which we have reason to consider as well founded. This is a circumstance which chemists often neglect, though it is of the highest importance; and without attending to it, we cannot expect to make any valuable improvement in the theory of chemistry. Long custom is necessary, and a very extensive acquaintance indeed with chemistry, to have, so to speak, the whole science before our eyes, in order to be able to judge, without long reflection, whether an ingenious explanation of some phenomenon be inconsistent or not with some other part of the theory. It is from not attending to this circumstance, that chemists of the greatest distinction sometimes adopt ideas respecting some points, which are inconsistent with other opinions equally adopted by them.

I shall here give an example of this. Dr. Thomson, whose merits as a skilful chemist do not stand in need of any panegyric from me, has examined, (*Annals of Philosophy*, iii. 139,) the laws relating to the combination of oxides with each other; an examination for which chemists are much obliged to him. He then says, "the more I have examined this law, the more correct in general does it appear." In the same volume, page 106, speaking of *iodine*, this philosopher expresses himself as follows: "How much these new discoveries must alter the presently received chemical theory, and how they serve to confirm Davy's opinion respecting muriatic acid, is too obvious to escape attention." But had the author at this moment called to his mind the constitution of the submuriates with water of combination, he would have found that the laws concerning the combination of oxides, and the theory of Davy respecting muriatic acid, are absolutely irreconcilable; and that either the one or the other of these must be abandoned as erroneous. If, at this time, the external resemblance of crystallized iodine to the oxide of manganese crystallized had recalled the last of these to his mind, he would perhaps have found, that it is not more difficult to conceive how the first disengages an excess of oxygen to combine with the bases, than

how the last disengages an excess of oxygen to combine with the acids.*

But I have allowed myself perhaps to be carried too far by ideas which have spontaneously followed each other in my mind. I hope, however, that I have drawn the attention of the reader to circumstances which may be of some importance in the examination of chemical proportions, as well as in the theory of chemistry in general.

Section II

SCEPTICISM ABOUT THE VALUE OF THE THEORY

Wollaston had supported Dalton's theory, and had used it to explain both the laws of chemical combination and the structure of crystals. But in his paper of 1814 he turned against it, advising the use of 'equivalents', which had a secure empirical basis, in place of 'atomic weights'. The slide-rule device for calculating equivalents was widely used; and chemists generally followed Wollaston and used equivalents, even though they sometimes called them atoms. Chemists still use 'equivalents' and 'normal solutions', to the mild confusion of beginners, probably not usually realising that equivalents were introduced as competitors to atoms.

The rules for the Royal Medals of the Royal Society were waived so that Dalton could be given one of the first two, although his important work had been done twenty years earlier. Humphry Davy, as President, gave an address full of somewhat equivocal praise for Dalton and his theory. Davy was a strange and enigmatic man, who had risen from obscure origins to be Professor at the Royal Institution in London, and a Fellow of the Royal Society, in his early twenties; and President of the Society at forty-one. In dazzling bursts of creative work he had transformed the science of chemistry in the first decade and a half of the nineteenth century. Applying the voltaic battery to analysis, he discovered whole new families of elements, and suggested that the chemical bond was electrical. He then proved that chlorine had as much right to be counted as an element as any other substance on the list; thereby overthrowing Lavoisier's oxygen theory of acids. He proposed in its place the hydrogen theory of acids. He was consistently opposed to Dalton's theory, for reasons which will become clearer in Section III; there is no reason to believe that jealousy was involved, for contemporaries would have ranked Dalton far below Davy.

William Whewell, Master of Trinity College, Cambridge, was one of the great pundits of early Victorian England. An authority on subjects ranging from mineralogy through mathematics to moral philosophy, he did not hesitate in discussing atomism to play the gadfly. In his general view of the sciences, he

opposed the 'Baconian' school represented by J. S. Mill, who suggested that scientists proceeded by building up generalisations inductively from observations. Whewell preferred to stress the manner in which we impose our categories upon the world; and looked for metaphysical and *a priori* assumptions concealed beneath the surface of empirical-seeming treatises. Atomism seemed a good example of such an assumption, which had no connexion with empirical facts.

It is perhaps wrong to include Justus von Liebig in this section, for he was certainly an atomist of a kind. But he used the terms 'atom' and 'equivalent' as synonyms, and adhered, in the tradition stemming from Wollaston, to an atomic theory from which hypothesis was excluded. The *Familiar Letters on Chemistry* began as a slim volume; it was extremely successful, and in later editions further letters were added. Liebig was one of the foremost chemists of his generation, and is best known for introducing systematic laboratory work into his courses at Giessen. He was not the first ever to do so, but it was his example which caught on and transformed the teaching of chemistry. His main field of research was organic chemistry, particularly the application of chemistry to agriculture and to physiology. In the letter reprinted here, Liebig compared the use in chemistry of the terms 'atom' and 'element', both of which represented, according to him, empirical limits and no more.

FURTHER READING

- W. H. Brock (ed.), *The Atomic Debates*, Leicester, 1967
H. Hartley, *Humphry Davy*, London, 1966

PHILOSOPHICAL TRANSACTIONS.

I. *A Synoptic Scale of Chemical Equivalents.* By William Hyde Wollaston, M. D. Sec. R. S.

Read November 4, 1813.

WHEN the nature of any saline compound is proposed as the subject of inquiry to an analytic chemist, the questions that occur for his consideration are so varied and so numerous, that he will seldom be disposed to undertake a series of original experiments for the purpose of satisfying his inquiries, so long as he can rely upon the accuracy of those results that have been obtained by the labour of others, who have preceded him in this field of patient investigation.

If, for instance, the salt under examination be the common blue vitriol, or crystallized sulphate of copper, the first obvious questions are, (1) How much sulphuric acid does it contain? (2) How much oxide of copper? (3) How much water? He may not be satisfied with these first steps in the analysis, but may desire to know further the quantities (4) of sulphur, (5) of copper, (6) of oxygen, (7) of hydrogen. As means of gaining this information, he naturally considers the quan-

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tities of various reagents that may be employed for discovering the quantity of sulphuric acid, (8) how much barytes, (9) carbonate of barytes, or (10) nitrate of barytes, would be requisite for this purpose; (11) How much lead is to be used in the form of (12) nitrate of lead; and when the precipitate of (13) sulphate of barytes or (14) sulphate of lead are obtained, it will be necessary that he should also know the proportion which either of them contains of dry sulphuric acid. He may also endeavour to ascertain the same point by means of (15) the quantity of pure potash, or (16) of carbonate of potash requisite for the precipitation of the copper. He might also use (17) zinc or (18) iron for the same purpose, and he may wish to know the quantities of (19) sulphate of zinc, or (20) sulphate of iron that will then remain in the solution.

These, and very many more questions of the same kind, which it would be tedious to specify, and needless to enumerate, engage the thoughts, and will occupy much of the time of every experimental chemist, unless he can have recourse to some record of former analyses on which he can depend.

The scale, which I am about to describe, is designed to answer at one view all these questions, with reference to most of the salts contained in the table, not merely expressing numerically the proportions by which the desired answers may be calculated, but directly indicating the actual weights of the several ingredients, contained in any assumed weight of the salt under consideration, and also the actual quantities of several reagents that may be used, and of the precipitates that would be obtained by each.

In the formation of this scale, it is requisite in the first place

to determine the proportions in which the different known chemical bodies unite with each other, and to express these proportions in such terms that the same substance shall always be represented by the same number.

It is to RICHTER that we are originally indebted for this mode of expression, and for having first observed that law of permanent proportions on which the possibility of this numerical representation is founded. The proportions assigned to various salts by his predecessors BERGMAN, WENZEL, KIRWAN, were incompatible with this mode of notation. If we turn to BERGMAN's treatise *De Analysi Aquarum*, we find it stated that in sulphate of potash 40 of acid are combined with 52 of potash, or that 100 of sulphuric acid take 130 of potash. In muriate of potash, 61 of the alkali are said to be combined with 31 of acid, which is in the proportion of 130 to 66. So that the same quantity of potash that is saturated by 100 sulphuric acid, requires of muriatic 66.

But if we make a similar estimate by means of lime, since sulphate of lime is said to contain 46 acid combined with 32 lime, 100 of acid would require 69,5. And in muriate of lime, since 44 of lime are said to be combined with 31 of acid, thence 69,5 of lime would require 49. So that in this instance it would appear that the equivalent to 100 sulphuric acid, instead of being 66 muriatic, is 49; which, if true, would defeat our attempts to express the same body always by the same number.

In comparing the analyses of WENZEL with each other, we find the same inconsistency. If we select sulphate of ammonia, and muriate of ammonia, we obtain 67,3 as the equivalent of muriatic acid. But by comparison of sulphate of magnesia

with muriate of magnesia, it would appear to be 73 instead of 67,3.

In recurring to the tables of KIRWAN, a similar obstacle presents itself to the determination of the quantity of muriatic acid, that is equivalent to a given weight of sulphuric acid. When the comparison is made by means of potash, the result would make it appear that 68,3 is the relative weight of muriatic acid. But, if the compounds of these acids with lime be employed in the computation, the result instead of 68,3 gives only 59.

RICHTER remarked, on observing this sort of inconsistency, that if sulphate of potash formed according to the proportions of KIRWAN were decomposed by muriate of lime, there should be found a large excess of alkali in the solution. But, on the contrary, by direct experiment he found that neutral salts, when mixed, remained in all cases neutral, and consequently, that the same weight of muriatic acid would in all cases be found equivalent to the same quantity of sulphuric acid; and therefore might be conveniently expressed in stating the composition of salts, by the same number. He estimates this acid at 712, as the equivalent to 1000 dry sulphuric acid, the number assumed as his standard of comparison, to which all other numbers for acids, alkalies, and earths are adapted.

It could not escape the penetration of M. BERTHOLLET, that there exist numerous deviations from this law of neutralization, and cases of prevailing affinity dependent on a redundancy of one or other ingredient in a mixture of salts. But he was not so happy in detecting the definite law, by which many, at least, of these deviations are governed. It has since been found, that when a base unites with a larger portion of acid

than is sufficient to saturate it, the quantity combined is then an exact simple multiple of the former, thus exhibiting a new modification of the law of definite proportions, rather than any exception to it.

The first instance in which the same body was supposed to unite with different doses of another, in such proportions that one of these doses is a simple multiple of the other, was noticed by Mr. HIGGINS, who conceived, rather than actually observed to occur, certain successive degrees of oxidation of azote, and represented the series of its combinations with oxygen to be

* Azote 1 with 2 oxygen making nitrous gas.

Azote 1 with 3 oxygen making red nitrous vapour.

Azote 1 with 4 oxygen making yellow nitrous acid.

Azote 1 with 5 oxygen making white nitric acid.

He at the same time added his opinion, that such are the proportions in which these gases unite to each other by *bulk*, having before observed one instance of union by exactly double bulk in the formation of water by the combustion of hydrogen and oxygen, and expressed his persuasion that the number of particles in a given bulk of the different gases is the same, and that the number of particles in the compounds of azote and oxygen, are successively in the proportions above stated.

But though Mr. HIGGINS, in the instance of the union of hydrogen with oxygen, anticipated the law of bulks observed by M. GAY LUSSAC, with respect to the union of gases, and in his conception of union by ultimate particles clearly preceded Mr. DALTON in his atomic views of chemical combination, he appears not † to have taken much pains to ascertain

* A comparative View of the phlogistic and antiphlogistic theories, 1789, p. 133.

† In straw coloured nitrous acid, the proportion *appears* to be four to one; but

the actual prevalence of that law of multiple proportions by which the atomic theory is best supported, and it is in fact to Mr. DALTON that we are indebted for the first correct observation of such an instance of a simple multiple in the union of nitrous gas with oxygen. In his endeavours to determine the composition of the atmosphere, he found that the quantity of oxygen contained in 100 measures of common air would combine with either 36 or 72 measures of nitrous gas, according to certain variations in the mode of conducting the experiment.*

Chemists in general, however, appear to have been by no means duly impressed with the importance of this observation of Mr. DALTON, till they were in possession of other facts observed by Dr. THOMSON and myself,† in a more tangible form, with regard to neutral and superacid or subacid salts, which could be made the subjects of more deliberate and less equivocal experiments; and it is, perhaps, owing to the repetition and confirmation of them by M. BERTHOLLET,‡ that they have attracted the attention of other chemists, who are now ready to admit that the term binacid correctly expresses the relation of many superacid salts to neutrals consisting of the same ingredients. Since that time the additional instances in which the same law has been observed to prevail, are become so numerous, especially with regard to different degrees of oxidation, that we have the greatest reason to presume that

the colourless contains *about* five of dephlogisticated to one of phlogisticated air. Comparative View, p. 84.

* Manchester Mem. Vol. V.—NICH. Journal, Vol. XIII. p. 433.

† Phil. Trans. 1808, p. 74.—Ditto, p. 96.

‡ Mem. d'Arcueil, Tome II. p. 470.

it is universal, and that in such analyses as are found not to accord with this general observation, we are warranted in suspecting some degree of inaccuracy in one or other of the results compared together.

According to Mr. DALTON's theory, by which these facts are best explained, chemical union in the state of neutralization takes place between single atoms of the substances combined; and in cases where there is a redundance of either ingredient, then two or more atoms of this kind are united to only one of the other.

According to this view, when we estimate the relative weights of equivalents, Mr. DALTON conceives that we are estimating the aggregate weights of a given number of atoms, and consequently the proportion which the ultimate single atoms bear to each other. But since it is impossible in several instances, where only two combinations of the same ingredients are known, to discover which of the compounds is to be regarded as consisting of a pair of single atoms, and since the decision of these questions is purely theoretical, and by no means necessary to the formation of a table adapted to most practical purposes, I have not been desirous of warping my numbers according to an atomic theory, but have endeavoured to make practical convenience my sole guide, and have considered the doctrine of simple multiples, on which that of atoms is founded, merely as a valuable assistant in determining, by simple division, the amount of those quantities that are liable to such definite deviations from the original law of RICHTER.

Having some time since computed for private use a series of supposed atoms, I had assumed oxygen as the decimal unit of my scale, in order to facilitate the estimation of those

numerous combinations which it forms with other bodies. But, though in the present table of Equivalents, I have retained the same unit, and have taken care to make oxygen equally prominent for the same reason as before, as well as on account of the important part it performs in determining the affinities of bodies by the different proportions in which it is united to them; nevertheless the real measure, by which most bodies are compared to each other, in any experiments that I have made, and to which I have, in fact, endeavoured to find equivalents, is a determinate quantity of carbonate of lime. This is a compound, that may be regarded as most distinctly neutral. It is most easy to obtain in a state of uniform purity; most easy to analyse (as a binary compound); it is a most convenient measure for the powers of acids, and affords the most distinct expression for the comparative neutralizing powers of alkalies.

The first question, consequently, to be resolved is, by what number are we to express the relative weight of carbonic acid, if oxygen be fixed at 10. It seems to be very well ascertained, that a given quantity of oxygen yields exactly an equal measure of carbonic acid by union with carbon; and since the specific gravities of these gases are as 10 to 13.77,* or as 20 to 27.54, the weight of carbon may be justly represented by 7.54, which, in this instance, is combined with 2 of oxygen forming the deutoxide, and carbonic oxide being the protoxide will be duly represented by 17.54.

Carbonic acid having consequently been assumed as 27.54 it follows from the analysis of carbonate of lime, which by heat loses 43.7 per cent. of acid, and leaves 56.3 of base, that they

* BIOT and ARAGO 1,1036 : 15196 :: 10 : 13.77.

are combined in the proportion of 27,54 to 35,46, and consequently that lime must be represented by 35,46, and carbonate of lime by 63.

If I would proceed in the series for the purpose of estimating the reliance to be placed on preceding analyses, I might dissolve 63 of carbonate of lime in muriatic acid, and by evaporating to perfect dryness should obtain about 69,56* muriate of lime, and by deducting the weight of the lime 35,46 should learn, by means of the difference 34,1, what is to be considered as dry muriatic acid.

But since lime is now known, by the brilliant discoveries of Sir H. DAVY, to be a metallic body united with oxygen, this salt may also be viewed as a binary compound in a different light as oxymuriate of calcium; in which case we must transfer the weight of 10 oxygen to the muriatic acid, making 44,1 of oxymuriatic acid combined with 25,46 calcium. Or, lastly, if with the same distinguished chemist, we regard it as chlorid of calcium, its place in the scale of equivalents is the same 69,56, and the portion of matter here added to the calcium, whether it retain its late name of oxymuriatic acid, or revert to its original one of dephlogisticated marine acid, or assume its new one of chlorine, will be rightly represented by 44,1, which expresses a bare fact without reference to any theory, and affords the means of estimating the proportion of this constituent in all muriatic compounds, without need of controversy respecting its simple or compound nature, which may

* In Dr. MARCET's experiments on the composition of muriate of lime, referred to in his Analysis of the Water of the Dead Sea,

50,77 carbonate gave 56,1 of muriate of lime,

and 50,77 : 56,1 :: 63 : 69,6.

never admit of any argument that will be deemed conclusive by all parties.

With the same latitude of interpretation may be understood muriate of potash or of soda in the scale of equivalents; and the relative weights of mere potash or soda may, perhaps, be determined better by means of these compounds than by any other, because they are not liable to be superacid, and are not decomposed by heat.

If to a quantity of muriatic acid, which, by previous trial, I know would dissolve 100 carbonate of lime, I add 100 grains of crystallized carbonate of potash, and after the addition find that it will dissolve only 49,8 of carbonate of lime; I hence infer that 100 of this carbonate is equivalent to 50,2 carbonate of lime, and consequently that 125.5 is the equivalent to 63 in the table.

Next, if I combine 125.5 of crystallized carbonate of potash with an excess of muriatic acid, and evaporate to dryness, I expel the whole of the water with all redundant acid, and I find 93,2 of neutral salt; and whether I call it muriate of potash, or chlorid of potassium, or by any other name, with any other views, I may deduct 34,1 as dry muriatic acid, (whether real or imaginary*) and infer the equivalent for potash to be 59,1, even though there should, in fact, be only 49,1 of potassium present, requiring 10† of oxygen to convert it into potash.

* Its separate existence is certainly imaginary, for it can no more be obtained uncombined than dry sulphuric acid, or dry nitric acid.

† If all the steps in the series, by which the number 49,1 is inferred, be correct, this should be exactly 10,00 without any fraction; and the proportion assigned to muriate of potash by BERZELIUS is sufficiently near, to shew that there can be no considerable error. $83,02 : 16,58 :: 49,1 : 10,04$.

The next question that occurs relates to the composition of this crystallized carbonate of potash, which I am induced to call bi-carbonate of potash, for the purpose of marking more decidedly the distinction between this salt and that which is commonly called a subcarbonate,* and in order to refer at once to the double dose of carbonic acid contained in it. With reference to carbonate of lime also, I must necessarily consider it as a supercarbonate, for if I add a solution of this salt to a neutral solution of muriate of lime, a considerable effervescence takes place, from a redundancy of carbonic acid beyond what is necessary to saturate the lime. If I saturate 125,5 of this salt with nitric acid, taking due precautions not to expel any of the fluid along with the gas which escapes, it loses about 55 of carbonic acid, which is the double of 27,5. But if, previous to the saturation, I heat the salt moderately red, it loses 38,8, consisting of 27,5 carbonic acid and 11,3 water, after which the addition of an acid expels only 27,5, or a single dose of carbonic acid.†

I have in this experiment made use of nitric acid, in order that the resulting compound might guide me in the selection from among former estimates which are extremely discordant with regard to the equivalent of that acid. The proportion of nitrate of potash, which I have obtained by evaporating such a solution by a heat just sufficient to fuse the residuum, gave at the lowest in three experiments 126, for the equivalent of nitrate of potash; from which, if we deduct 59,1 potash,

* I avoid using the term carbonate of potash for either of these salts, because it has been applied to both, and consequently is liable to be misunderstood when standing alone.

† Phil. Trans. 1808, p. 97.

there will remain 66 g as the apparent equivalent of dry nitric acid. Consequently, I have no hesitation in preferring the estimate * to be obtained from RICHTER's analysis of nitrate of potash, which gives 67.45, from which if we subtract one portion of azote 17.54, there remain 49.91, so nearly 5 portions of oxygen, that I consider the truth to be $17.54 + 50$, or 67.54.

From this sketch of the mode in which such an inquiry may be pursued, wherever it is necessary to make any original experiments, it will be fully understood what is meant by equivalents, and in what manner the series might be continued. I have, however, in most instances drawn my inferences from former analyses, and indeed in all, where I could find coincidences between different authorities sufficient to give confidence in their results.

But with respect to oxalic acid, I again found a difficulty in deciding among the discordant results of different analyses, and was obliged to have recourse to direct experiment.

100 grains of bin-oxalate of potash (commonly called salt of sorrel) were subjected to a degree of heat sufficient to destroy the oxalic acid, and to convert the salt into a subcarbonate of potash. A quantity of muriatic acid was then poured on this residuum, and afterwards saturated with carbonate of lime; and an equal quantity of the same acid was saturated with carbonate of lime alone. By the excess of carbonate dissolved in the latter instance, it was found that 100 bin-oxalate was equivalent to 40.9 carbonate of lime; and hence the equivalent to 6g carbonate of lime will be 154 of the bin-oxalate of potash. After deducting 59.1 potash, the remainder

* $46.7 : 53.3 :: 59.1 : 67.45$ quoted in *Mem. d'Arcueil*, II. 59.

94.9 divided by 2, gives 47.45 for the equivalent of dry oxalic acid. I therefore again adopt the result of the very industrious and ever accurate BERZELIUS, obtained by means of oxalate of lead, that 296.6* litharge are combined with 100 oxalic acid, which are in the proportion of 139.5 litharge to 47.0 oxalic acid. Such a degree of accordance between methods totally different appears highly satisfactory, and seems to shew that in attempts to determine the same point by means of lime, some compounds may possibly be formed at the same time differing in the proportions of acid and base, as in the cases of oxalate and bin-oxalate of strontia, observed by Dr. THOMSON, and that erroneous inferences may have been drawn from precipitates in which they are blended.

With the exception of those instances that I have enumerated, there are few in which I have found it necessary to make any new experiments, as I have met with coincidences between the independent results of others sufficient to satisfy me of their correctness; and accordingly I have adopted such determinations without any pretensions to improve upon them by new experiments of my own.

It is not my design in the table which follows this paper, to attempt a complete enumeration of all those elements or compounds which I suppose to be well ascertained, but merely to include some of those which most frequently occur. I do not offer it as an attempt to correct the estimates that have been formed by others, but as a method in which their results may be advantageously applied in forming an easy approximation to any object of our inquiries.

The means by which this is effected may be in part understood by inspection of the Plate I., in which will be seen the

* Ann. de Chimie, No. 243.

list of substances intended to be estimated, arranged on one or the other side of a scale of numbers in the order of their relative weights, and at such distances from each other, according to their weights, that the series of numbers placed on a sliding scale can at pleasure be moved, so that any number expressing the weight of a compound may be brought to correspond with the place of that compound in the adjacent column. The arrangement is then such, that the weight of any ingredient in its composition, of any reagent to be employed, or precipitate that might be obtained in its analysis, will be found opposite to the point at which its respective name is placed.

In order to shew more clearly the use of this scale, the Plate exhibits two different situations of the slider, in one of which oxygen is 10, and other bodies are in their due proportion to it, so that carbonic acid being 27,54, and lime 35,46, carbonate of lime is placed at 63.

In the second figure, the slider is represented drawn upwards till 100 corresponds to muriate of soda; and accordingly the scale then shews how much of each substance contained in the table is equivalent to 100 of common salt. It shews, with regard to the different views of the analysis of this salt, that it contains 46,6 dry muriatic acid, and 53,4 of soda, or 39,8 sodium, and 13,6 oxygen; or if viewed as chlorid of sodium, that it contains 60,2 chlorine, and 39,8 sodium. With respect to reagents, it may be seen that 283 nitrate of lead, containing 191 of litharge employed to separate the muriatic acid, would yield a precipitate of 237 muriate of lead, and that there would then remain in solution nearly 146 nitrate of soda. It may at the same time be seen, that the acid in this quantity of salt would serve to make 232 corrosive sublimate contain-

ing 185,5 red oxide of mercury, or would make 91,5 muriate of ammonia, composed of 6 muriatic gas (or hydromuriatic acid) and 29,5 ammonia. The scale shews also, that for the purpose of obtaining the whole of the acid in distillation the quantity of oil of vitriol required is nearly 84, and that the residuum of this distillation would be 122 dry sulphate of soda, from which might be obtained, by crystallization, 277 of GLAUBER salt containing 155 water of crystallization. These and many more such answers appear at once by bare inspection, as soon as the weight of any substance intended for examination is made by motion of the slider correctly to correspond with its place in the adjacent column.

With respect to the method of laying down the divisions of this scale, those who are accustomed to the use of other sliding-rules, and are practically acquainted with their properties, will recognise upon the slider itself the common GUNTER'S line of numbers, (as it is termed) and will be satisfied that the results which it gives are the same that would be obtained by arithmetical computation.

Those who are acquainted with the doctrine of ratios, and with the use of logarithms as measures of ratios, will understand the principle on which this scale is founded, and will not need to be told that all the divisions are logometric, and consequently that the mechanical addition and subtraction of ratios here performed by juxta-position, corresponds in effect to the multiplication and division of the numbers by which those ratios are expressed in common arithmetical notation.

To others who are not equally conversant with the nature of logarithms, and consequently have not so correct a conception of the magnitudes of ratios, some further explanation of

the mode in which the scale of equivalents is constructed, will, I presume, be acceptable.

They will observe, that the series of natural numbers are not placed at equal intervals on the scale; but that at all equal intervals are found numbers which bear the same proportion to each other. In fig. 3, some of the larger intervals alone are represented on a line similarly divided. The succession of intervals, marked A, B, C, D, E, are all equal, and at these points of division are placed numbers 1, 2, 4, 8, 16, which increase progressively by the same ratio. And since the series $3 : 6 : 12 : 24$ increase in the same ratio of 1 to 2, these intervals *a, b, c, d, e*, are the same as the former. At another succession of different yet equal intervals, marked F, G, H, I, are placed numbers 1, 3, 9, 27, which increase regularly by an equal ratio of 1 to 3; and by means of a pair of compasses it would be found that the interval from 2 to 6, or from 6 to 18 (which are in the same ratio of 1 to 3,) is exactly equal to FG, the interval between 1 and 3. As any single space represents any one ratio, so the sum of any 2 or 3 equal spaces represent a double or triple ratio. If 1 be increased three times by the ratio of 1 to 2, it becomes 8, which bears to 1 triple the ratio of 2 to 1. This ratio is therefore rightly represented by AD, which is the triple of AB.

The distances of the intermediate numbers 5, 7, 10, 11, 13, &c. from 1 are likewise made proportional to the ratios which they bear to 1, and are easily laid down by means of a table of logarithms; for as these are arithmetic measures of the ratios which all numbers bear to unity, the spaces proportional to them become linear representations of the same quantities.

As the entire spaces AD, AE represent the ratios of 8 and of 16 respectively to 1, so the difference DE represents the ratio of 8 and 16, which stand at D and E, to each other. And in the same manner, any other space *kl* represents correctly the ratio of 7 to 13; so that the measure of a fraction expressed by quantities that are incommensurate is rendered as obvious to sight, as that of any simple multiple. And if a pair of compasses be opened to this interval, and transferred to any other part of the scale, the points of the compasses will be found to rest upon numbers bearing the same proportion to each other as those from which the interval was transferred.

It is exactly in this manner, that the various points in the column of equivalents indicate the several quantities sought in any given position of the slider. The relative distances, at which the articles are placed, represent so many different openings of the compasses rendered permanent and presented to view at once. In the table, which I shall place at the end of this communication, the relation of the various substances enumerated to each other is expressed by numbers. In the engraved scale of equivalents, the ratios of these numbers are represented by logometric intervals at which they are placed, their several positions being determined by those of their respective numbers on the slider, which is logometrically divided. Consequently all the several points in the column of equivalents will indicate numbers in the same due proportions to each other, whatever part of the scale may be presented to them. Those who seek information may obtain it by inspection; those who already possess it, may be able to correct the positions of some articles by direct comparison with the best

analyses upon record, in whatever numbers the results of those analyses may happen to be expressed.

I hope, that without trespassing too much on the time of the Society, I shall have rendered the principle and practical use of this scale intelligible. I trust, that it will prove useful as an assistant to chemists in general. It will at least serve for a specimen of the extreme facility of mechanical approximation, which may very frequently be advantageously substituted for computations, that are often more laborious than the accuracy of our data warrants; and if it tend to introduce into more general use, that valuable instrument the common sliding-rule, it will be the means of saving no inconsiderable portion of time to those who are engaged in scientific pursuits.

Numerical Table of Equivalents.

Hydrogen	-	(a)	1,32				
Oxygen	-	-	10,00				
Water	-	-	11,32				
Carbon	-	(b)	7,54 + 20	Oxygen = 27,54	Carbonic acid.		
Sulphur	-	(f)	20,00 + 30	Oxyg. = 50	Sulphuric acid.		
Phosphorus	-	(g)	17,40 + 20	Oxyg. = 37,4	Phosphoric acid.		
Azote	-	(o)	17,54 + 50	Oxyg. = 67,54	Nitric acid (q).		
Muriatic Acid (dry)	(e)	34,1 + 10	Oxyg. = 44,1	Oxymuriatic acid.			
Chlorine	-	-	44,1 = Oxymur. acid + 1,32	Hydrog. = 45,42	Muriatic gas.		
Oxalic acid	-	(b)	47,0				
Ammonia	-	(p)	21,5				
Soda	-	(l)	39,1 - 10	Oxyg. = 29,1	Sodium.		
Potash	-	(m)	59,1 - 10	Oxyg. = 49,1	Potassium.		
Magnesia	-	(n)	24,6				
Lime	-	(c)	35,46 - 10	Oxyg. = 25,46	Calcium.		
Strontia	-	(k)	69,				
Barytes	-	(i)	97,				
Iron	-	(r)	34,5 + 10	Oxyg. = 44,5	Green Oxid of Iron.		
			+ 15	Oxyg. = 49,5	Red Oxid.		

Copper	-	(t)	40,	+ 10	Oxyg.	= 50,	Black Oxid of Copper.
Zinc	-	(s)	41	+ 10	Oxyg.	= 51,	Oxid of Zinc.
Mercury	-	(v)	125,5	+ 10	Oxyg.	= 135,5	Red Oxid Mercury.
						+ 125,5	8 = 261 Protoxid 8.
Lead	-	(d)	129,5	+ 10	Oxyg.	= 139,5	Litharge.
Silver	-	(u)	135,	+ 10	Oxyg.	= 145,	Oxid Silver in Muriate.
Subcarb. of Ammonia			49,0	+ 27,5	C. acid	= 76,5	Bi-Carb. of Ammonia.
Subcarb. of Soda	-		66,6	+ 27,5	C. acid + 11,3	Water = 105,5	Bi-Carb. of Soda.
Subcarb. of Potash	-		86,	+ 27,5	C. acid + 11,3	Water = 125,5	Bi-Carb. of Potash.
Carbonate of Lime			63				
----- Barytes	-		124,5				
----- Lead	-		167,				
Sulphuric acid (dry)			50,	+ 1	Water 11,3	= 61,3	Oil of Vitriol (sp. gr. 1,85).
Sulphate of Soda	-		89,1	+ 10	Water 113,2	= 202,3	Glauber Salt.
----- Potash	-		109,1				
----- Magnesia (n)			74,6	+ 7	Water 79,3	= 153,9	Epsom Salt.
----- Lime			85,5	+ 2	Water 22,64	= 108,1	Selenite.
----- Strontia	-		119,0				
----- Barytes	-		147,0				
----- Copper	-		156,6	= 1	Acid + 1 Oxid. + (w) 5	Water 56,6.	
----- Iron	-		173,8	= 1	Acid + 1 Oxid. + 7	Water 79,3.	
----- Zinc	-		180,2	= 1	Acid + 1 Oxid. + 7	Water 79,3.	
----- Lead	-		189,5				
Nitric acid (dry)	(q)		67,54	+ 2	Water 22,64	= 90,2	Liquid Nitric acid (sp. gr. 1,50)
Nitrate of Soda	-		106,6				
----- Potash	-		126,6				
----- Lime	-		103,0				
----- Barytes	-		164,5				
----- Lead	-		207,0				
Muriate of Ammonia	-		66,9	= 1	Acid + 1 Amm. + 1	Water.	
----- Soda	-		73,2				
----- Potash	-		93,2	+ 60	Oxygen = 153,2	Hyper-Oxymuriate of Potash.	
----- Lime	-		69,6				
----- Barytes	-		131,0	+ 2	Water 22,6 (w) 153,6	Crystallized Mur. Barytes.	
----- Lead	-		173,6				
----- Silver	-		179,1				
Corrosive Sublimate	-		170,1	= 1	Acid 1 Oxyg. + 1	Mercury.	
Calomel	-		296,1	= 1	Acid + 1 Oxyg. + 2	Mercury.	
Phosphate of Lead	-		176,9				
Oxalate of Lead	-		186,5				
Bin-Oxalate of Potash			153,0	= 2	Acid + 1	Potash	

Data on which the Table is founded.

Composition of Water	(1) 88,286 : 11,714 :: Oxygen	10	:	10,00 1,327	Oxygen Hydrogen (a)
				11,327	Water
Specific Gravities	- (2) 1,1036 : 1,5196 :: 2 Oxygen	20	:	27,54	Carbonic acid (b)
Carbonate of Lime	(3) 43,7 : 56,3 :: Carb. acid	27,54	:	35,46	Lime (c)
Carbonate of Lead	(4) 16,5 : 83,5 :: Carb. acid	27,54	:	139,5 10	Litharge
				129,5	
Litharge	- (5) 7,15 : 92,85 :: Oxygen	10	:	129,7	} Lead (d)
Muriate of Lime from	Carbonate of Lime (6) } 50,77 : 56,1 :: Carb. Lime	64	:	69,6	Mur. Lime
				Lime 35,5	
Muriate of Lead	- (7) 409,47 : 100 :: Litharge	139,5	:	34,1 34,1	} Muriatic acid (e)
Sulphate of Lead	- (8) 279 : 100 :: Litharge	139,5	:	50,0	Sulphuric acid
		3 Oxygen = 30			
Galena	- (9) 86,64 : 13,36 :: Lead	129,5	:	20	} Sulphur (f)
Ditto	- (10) 85,1 : 13 :: Lead	129,5	:	19,8	
Phosphate of Lead	(11) 380,56 : 100 :: Litharge	139,5	:	37,4	Phosphoric acid
		2 Oxygen 20			
Phosphoric acid	- (12) 53,28 : 46,72 :: Phosph. acid	37,4	:	17,4	Phosphorus (g)
Oxalate of Lead	- (13) 296,6 : 100 :: Litharge	139,5	:	47,0	Oxalic acid (h)
Carbonate of Barytes	(14) 100 : 352,57 :: Carb. acid	27,54	:	97	} Barytes (i)
Sulphate of Barytes	(15) 34 : 66 :: Sulph. acid	50	:	97	
Sulphate of Strontia	(16) 42 : 58 :: Sulph. acid	50	:	69	Strontia (k)
Common Salt	- (17) 134 : 88 :: Chlorine	44,1 10	:	29 10	Sodium (l)
Ditto	- (18) 100 : 114,78 :: Mur. acid	34,1	:	39,1	} Soda
Subcarbonate of Soda	(19) 41,24 : 58,76 :: Carb. acid	27,54	:	39,1	
Muriate of Potash	(20) 100 : 173,47 :: Mur. acid	34,1	:	59,1 10	Potash (m)
				49,1	Potassium
				44,1	
Muriate of Potash from	Potassium (21) } 32 : 60,8 :: Potassium	49,0	:	93,2	Mur. Potash
(1) Biot and Arago	(2) Ditto	(3) Experiment	(4) Berzelius	(5) Berzelius	
(6) Marcet	(7) Berzelius	(8) Berzelius	(9) Ditto	(10) Thomson	
(11) Berzelius	(12) Rose	(13) Berzelius	(14) Ditto	(15) Klaproth	
(16) Ditto	(17) Davy	(18) Berzelius	(19) Ditto	(20) and (21) Ditto	

of Chemical Equivalents.

21

Sulphate of Magnesia	(22)	67	:	33	::	Sulph. acid	50	:	24,6	Magnesia (n)		
									50			
									74,6			
Epsom Salt	100	-	(23)	51,5	:	48,5	::	7 Water	79,3	:	74,4	} Sulph. Magnesia
Specific Gravities	-	(24)	,07321	:	,96913	::	Hydrogen	1,327	:	17,54	Azote (o)	
									3 Hydrogen = 3 × 1,327		3,98	
Ammonia	-	(25)	1 Azote + 3 Hydrogen								21,52	} Ammonia (p)
Subcarb. Ammonia	-	(26)	56,02	:	43,98	::	Carb. acid	27,54	:	21,6		
Bi-carb. Ammonia	-	(27)	11,8	:	28,2	::	2 Carb. acid	55,1	:	21,6		
Nitrate of Potash	-	(28)	46,7	:	53,3	::	Potash	59,08	:	67,45		} Nitric acid (q)
Nitric acid	-	(29)	1 Azote + 5 Oxygen								67,54	
									2 Water = 2 × 11,32		22,64	
											90,18	} Liquid Nitric acid
Marble dissolved	-	(30)	476	:	681, $\frac{3}{4}$::	Carb. Lime	63	:	90,23	S. G. 1,50	
Oxid of Iron	-	(31)	22,5	:	77,5	::	Oxygen	10	:	34,5		} Iron (r)
										10		
Sulphate of Iron	-	(32)	28,9	:	25,7	::	Sulph. acid	50	:	44,5		} Oxid of Iron
Oxid of Zinc	-	(33)	24,41	:	100	::	Oxygen	10	:	41	Zinc (s)	
Black Oxid Copper	-	(34)	20	:	100	::	Oxygen	10	:	40		} Copper (t)
										10		
Sulphate of Copper	-	(35)	32	:	32	::	Sulph. acid	50	:	50		} Oxid of Copper
Muriate Silver	-	(36)	19,05	:	80,95	::	Mur. acid	34,1	:	145	Oxid of Silver	
										10		
											135	} Silver (u)
Horn Silver	-	(37)	24,5	:	75,5	::	Chlorine	44,1	:	136		
Sulphuret Silver	-	(38)	14,7	:	100	::	Sulphur	20	:	136		
Red Oxid of Mercury	-	(39)	8	:	100	::	Oxygen	10	:	125		} Mercury (v)
Ditto	-	(40)	30	:	380	::	Oxygen	10	:	126,6		
Corros. Sublimate	-	(41)	2 × 67	:	380	::	Chlorine	44,1	:	125,4		
											10	
Protoxid	-	(42)	1 Oxygen + 2 Mercury								262	} Protoxid y
Protoxid	-	(43)	4	:	104	::	Oxygen	10	:	260		
Calomel	-	(44)	11,5	:	88,5	::	Mur. acid	34,1	:	262		

(22) Henry	(23) by experiment	(24) Biot and Arago	(25) by Hypothesis	(26) Gay Lussac
(27) Berthollet	(28) Richter	(29) by Hypothesis	(30) R. Phillips	(31) Thenard
(32) Berzelius	(33) Gay Lussac	(34) Chenevix	(35) Proust	(36) Marcet
(37) Davy	(38) Wenzel	(39) Fourcroy and Thenard.		(40) Davy
(41) Davy	(42) by Synthesis	(43) Fourcroy	(44) Chenevix	

Water contained in crystallized Salts.

Sulphate of Copper	(45) 100	: 36,3	:: 156,6	: 56,8 = $5 \times 11,36$	} Water (w)
Sulphate of Iron -	(46) 100	: 45,4	:: 173,8	: 79,0 = $7 \times 11,28$	
Sulphate of Zinc -	(47) 100	: 44,3	:: 180,2	: 79,8 = $7 \times 11,40$	
Sulphate of Magnesia	(48) 100	: 51,5	:: 153,9	: 79,3 = $7 \times 11,33$	
Glauber Salt -	(49) 100	: 56	:: 202,3	: 113,1 = $10 \times 11,31$	
Muriate of Barytes -	(50) 100	: 14,8	:: 153,6	: 22,8 = $2 \times 11,48$	

(45) Berzelius
(50) Ditto.

(46) Ditto

(47) Lost by heat

(48) By heat

(49) Berzelius

In this table I have selected in most cases double evidence from different sources, in order that the inferences might receive confirmation from their concurrence. Number (29) may be noticed as a result anticipated from preceding data, and found to coincide with remarkable accuracy.

In the distillation of nitric acid from nitre, the whole of the acid may be obtained, if we employ enough of sulphuric acid to convert the residuum into bi-sulphate of potash. In this case each portion of potash, from which dry nitric acid is separated, will displace the water from two equivalent quantities of sulphuric acid, and each portion of nitric acid weighing 67,54 will be found combined with 22,64 of water. Hence 90,18 of liquid nitric acid so obtained should dissolve the equivalent 63 of carbonate of lime. And in fact, by an experiment carefully conducted on a large scale by Mr. PHILLIPS,* it appears that $681\frac{3}{4}$ of such acid did dissolve 476 of marble, which is in the proportion of 90,18 to 62,96, corresponding with the estimate within $\frac{1}{1500}$ part, a degree of coincidence rarely to be found even in the repetition of the same experiment by the most skilful analyst.

The specific gravity of this acid was found to be 1,50.

* Experimental Examination of the Pharm. Lond. by R. PHILLIPS.

Fig. 3.

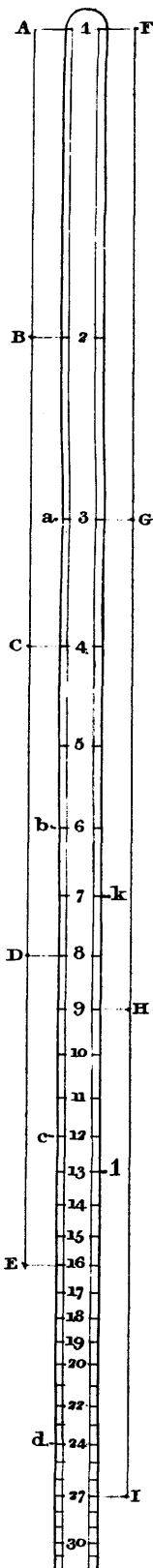


Fig. 2.

CHEMICAL	EQUIVALENTS
Oxygen	10
Water	11
10 Hydrogen	12
Phosphorus	13
2 Oxygen	14
Calcium	15
Sodium	16
3 Oxygen	17
Iron	18
Phosphoric acid	19
Copper	20
Chlorine	21
Muriatic gas	22
Oxalic acid	23
Sulphuric acid	24
5 Oxygen	25
Ox. Copper	26
2 Carbonic acid	27
6 Oxygen	28
Oil of Vitriol	29
(d) Nitric acid	30
Strontia	31
10 Carbon	32
Bi-Carb. Ammonia	33
Sub-Carb. Potash	34
Liquid Nitric acid	35
(S 6.150)	36
Barytes	37
(d) N. Lime	38
N. Soda	39
S. Potash	40
S. Strontia	41
Bi-Carb. Potash	42
Mercury	43
Lead	44
Silver	45
Litharge	46
Ox. Silver	47
Bin-Oxal. Potash	48
(60) Oxy. M. Potash	49
(c.5W) S. Copper	50
Corros. Sublimate	51
Phosph. Lead	52
Mur. Silver	53
S. Lead	54
(c.10W) S. Soda	55
2 Mercury	56
Protoacid &	57
Calomel (2 &)	58

Fig. 1.

CHEMICAL	EQUIVALENTS
Oxygen	10
Water	11
10 Hydrogen	12
Phosphorus	13
2 Oxygen	14
Calcium	15
Sodium	16
3 Oxygen	17
Iron	18
Phosphoric acid	19
Copper	20
Chlorine	21
Muriatic gas	22
Oxalic acid	23
Sulphuric acid	24
5 Oxygen	25
Ox. Copper	26
2 Carbonic acid	27
6 Oxygen	28
Oil of Vitriol	29
(S 6.150)	30
(d) Nitric acid	31
Strontia	32
10 Carbon	33
Bi-Carb. Ammonia	34
Sub-Carb. Potash	35
Liquid Nitric acid	36
(S 6.150)	37
Barytes	38
N. Lime	39
N. Soda	40
S. Potash	41
S. Strontia	42
Bi-Carb. Potash	43
Mercury	44
Lead	45
Silver	46
Litharge	47
Ox. Silver	48
Bin-Oxal. Potash	49
(60) Oxy. M. Potash	50
(c.5W) S. Copper	51
Corros. Sublimate	52
Phosph. Lead	53
Mur. Silver	54
S. Lead	55
(c.10W) S. Soda	56
2 Mercury	57
Protoacid &	58
Calomel (2 &)	59

ROYAL MEDALS.

You will recollect, Gentlemen, that the Right Honourable the Secretary of State for the Home Department,* who, I am happy to state, has, upon all occasions, shown his zeal to promote the interests of science, and of the Royal Society, announced at your Anniversary dinner, last year, his Majesty's gracious intention of founding two annual prizes, each of the value of fifty guineas, to be at the disposal of the President and Council of the Royal Society, for promoting the objects and progress of science, by awakening honourable competition amongst philosophers.

As this foundation was announced in the true spirit of royal munificence, so it has been completed with an exalted liberality, worthy of our august patron. The two prizes are established in the forms of silver and gold medals, to be given for important discoveries or useful labours in any department of science ; and they

* [Sir Robert Peel.]

are laid open to learned and ingenious men of all countries, without any principle of narrow policy or national exclusion.

In the first award of these royal medals, your Council have had some difficulties in their decision. Discoveries are sometimes made of great interest, which require time and new labours for their confirmation; and when their importance is great and their bearings extensive, years even may pass away, before a full conviction of their truth can be obtained. Now, though within the year just past, there have been more than one important discovery announced to the world, yet there are none which can be said to be, as yet, fairly and securely established.

Your Council, therefore, have rather looked to labours which have been sanctioned by time, the importance of which is generally felt, though not sufficiently acknowledged; which may be said to have acquired their full authority only within a very short period, and which, consequently, may be considered as within the literal meaning of the foundation.

I trust you will approve of the principle of the decision, and of the manner in which it has been made by your Council.

They have awarded the first prize to Mr. John Dalton, of Manchester, Fellow of this Society, for the Development of the Chemical Theory of Definite Proportions, usually called the Atomic Theory, and for his various other labours and discoveries in physical and chemical science.

What Mr. Dalton's merits are, I shall briefly endeavour to state to you, though it is impossible to do justice to them, in the time necessarily allotted to this address.

The brilliant and important discoveries of Black, Cavendish, Priestley, and Scheele, had added to chemistry a great variety of substances before unknown, many of which had forms never before witnessed in the material world; and the new and accurate logic of Lavoisier had assigned to many of them their just places in the arrangements of chemistry, and had established the characters of most of them, as simple or compound bodies. Novel uses of these substances were ascertained, new combinations of them made, and their applications to the purposes of common life, constantly extended by various distinguished chemists, in the close of the last century; but with respect to the weight or quantity in which the different elementary substances entered into union to form compounds, there were scarcely any distinct or accurate data. Persons, whose names had high authority, differed considerably in their statements of results, and statical chemistry, as it was taught in 1799, was obscure, vague, and indefinite, not meriting even the name of a science.

To Mr. Dalton belongs the distinction of first unequivocally calling the attention of philosophers to this important subject. Finding, that in certain compounds of gaseous bodies the same elements always combined in the same proportion; and that when there was more than one combination, the quantity of the elements always had a constant relation, such as 1 to 2, or 1 to 3 or to 4. He explained this fact, on the Newtonian doctrine of indivisible atoms, and contended that the relative weight of one atom to that of any other atom being known, its proportions or weight, in all its combinations, might be ascertained; thus making the statics of chemistry depend upon simple questions, in subtraction or multiplication, and enabling the student to de-

duce an immense number of facts, from a few well authenticated, accurate, experimental results.

I have said that to Mr. Dalton belongs the distinction of first unequivocally calling the attention of philosophers to this subject; but I should be guilty of historical injustice, if I did not state that various opinions and loose notions on the same mode of viewing the combinations of bodies, had existed before. And not to go back to the time of the Greek schools, to the Homoids of Anaxagoras, or to the Atoms of Epicurus, nor to those Newtonian philosophers who supported the permanency of atoms, and their uniform combinations, such as Keil, Freind, Hartley, and Marzucchi; there may be found in the works of Dr. Bryan Higgins, Mr. William Higgins, and Professor Richter, hints or conclusions, bearing decidedly on this doctrine. Dr. Bryan Higgins, in his *Experiments and Observations, relating to acetic acid, fixable air, dense, inflammable air, fire, and light*, published in 1786, contends that elastic fluids unite with each other in limited proportions only; and that this depends upon the combination of their particles or atoms, with the matter of fire which surrounds them as an atmosphere, and makes them repulsive of each other; and he distinguishes between simple elastic fluids, as composed of particles of the same kind, and compound elastic fluids, as consisting of two or more particles combined, in what he calls molecules, definite in quantity themselves, and surrounded by definite proportions of heat. Dr. Bryan Higgins' notions have, I believe, never been referred to by any of the writers on the Atomic Theory. Mr. William Higgins' claims have, on the contrary, often been brought forward. Yet, when it is recollected, that this gentleman was a pupil and relation of Dr. Bryan Higgins, and that his work, called

the *Comparative View*, was published some years after the treatises I have just quoted, and that his notions are almost identical (with the addition of this circumstance, that he mentions certain elastic fluids, such as the compounds of azote, consisting of 1, 2, 3, 4, and 5 particles of oxygen to one of azote,) it is difficult not to allow the merits of prior conception, as well as of very ingenious illustration, to the elder writer.

Neither of the Higgins attempted to express the quantities in which bodies combine by numbers; but Richter has a claim of this kind. In his *New Foundations of Chemistry*, published in 1795, he has shown that when neutro-saline bodies in general undergo mutual decompositions, there is no excess of alkali, earth, or acid; and he concludes that these bodies are invariable in their relation to quantity, and that they may be expressed by numbers.

Mr. Dalton, as far as can be ascertained, was not acquainted with any of these publications, at least he never refers to them: and whoever will consider the ingenious and independent turn of his mind, and the original tone prevailing in all his views and speculations, will hardly accuse him of wilful plagiarism. But let the merit of discovery be bestowed wherever it is due; and Mr. Dalton will be still pre-eminent in the history of the theory of definite proportions. He first laid down, clearly and numerically, the doctrine of multiples; and endeavoured to express, by simple numbers, the weights of the bodies believed to be elementary. His first views, from their boldness and peculiarity, met with but little attention; but they were discussed and supported by Drs. Thomson and Wollaston; and the table of chemical equivalents of this last gentleman, separates the practical part of the doctrine from the atomic or hypo-

thetical part, and is worthy of the profound views and philosophical acumen and accuracy of the celebrated author.

Gay Lussac, Berzelius, Dr. Prout, and other chemists, have added to the evidence in favour of the essential part of Mr. Dalton's doctrine; and for the last ten years it has acquired almost every month additional weight and solidity.

Gentlemen, I hope you will clearly understand that I am speaking of the fundamental principle, and not of the details, as they are found in Mr. Dalton's system of chemical philosophy. In many of these, the opinion of the composition of bodies is erroneous, and the numbers gained from first and rude experiments, incorrect; and they are given with much more precision in later authors on chemistry. It is in the nature of physical science, that its methods offer only approximations to truth; and the first and most glorious inventors are often left behind by very inferior minds, in the minutiae of manipulation; and their errors enable others to discover truth.

Mr. Dalton's permanent reputation will rest upon his having discovered a simple principle, universally applicable to the facts of chemistry—in fixing the proportions in which bodies combine, and thus laying the foundation for future labours, respecting the sublime and transcendental parts of the science of corpuscular motion. His merits, in this respect, resemble those of Kepler in astronomy. The causes of chemical change are as yet unknown, and the laws by which they are governed; but in their connexion with electrical and magnetic phenomena, there is a gleam of light pointing to a new dawn in science; and may we not hope that, in another century, chemistry having, as it were, passed

under the dominion of the mathematical sciences, may find some happy genius, similar in intellectual powers to the highest and immortal ornament of this Society, capable of unfolding its wonderful and mysterious laws.

I could with pleasure enter into a history of Mr. Dalton's other labours in chemical and physical science, but it would be impossible to give even an intelligible sketch of them, without occupying too much of the time which ought to be allotted to the other business of this day. His experiments, on the equal expansion of elastic fluids by heat, are allowed to be accurate, and their results well founded. His notions on the nature of the atmosphere, the mixture of gaseous bodies, and the distribution and communication of heat, and on the magnetic phenomena, display the resources of an ingenious and original mind; and his essays on evaporation, and the force of vapour, and the tests for discovering water in air, have offered important practical applications; but still their interest, though of a high kind, is inferior to that of the doctrine of definite proportions.

I trust you will allow the justice of the decision of your Council, which has claimed for our countryman this first testimony of royal benevolence to science.*

There is another motive which influenced them, and which I am sure will command your sympathy. Mr. Dalton has been labouring, for more than a quarter of a century, with the most disinterested views. With the greatest modesty and simplicity of character, he has remained in the obscurity of the country, neither asking for approbation, nor offering himself as an object of ap-

* [By a writer of some note this decision of the Council of the Royal Society in awarding the first royal medal to Mr. Dalton, has been called, by some unaccountable perversity of understanding, an insult to this distinguished man.]

plause. He is but lately become a Fellow of this Society; and the only communication he has given to you is one, compared with his other works, of comparatively small interest; their feeling on the subject, is therefore pure. I am sure he will be gratified by this mark of your approbation of his long and painful labours. It will give a lustre to his character, which it fully deserves; it will anticipate that opinion which posterity must form of his discoveries; and it may make his example more exciting to others, in their search after useful knowledge and true glory.

CHAPTER V.

THE ATOMIC THEORY.

1. *The Atomic Theory considered on Chemical Grounds.*—We have already seen that the combinations which result from chemical affinity are definite, a certain quantity of one ingredient uniting, not with an uncertain, but with a certain quantity of another ingredient. But it was found, in addition to this principle, that one ingredient would often unite with another in different proportions, and that, in such cases, these proportions are multiples one of another. In the three salts formed by potassa with oxalic acid, the quantities of acid which combine with the same quantity of alkali are exactly in the proportion of the numbers 1, 2, 4. And the same rule of the existence of multiple proportions is found to obtain in other cases.

It is obvious that such results will be accounted for, if we suppose the base and the acid to consist each of definite equal particles, and that the formation of the salts above mentioned consists in the combination of one particle of the base with one particle of acid, with two particles of acid, and with four particles of acid, respectively. But further; as we have already stated, chemical affinity is not only definite, but reciprocal. The proportions of potassa and soda which form neutral salts are 590 and 391 in one case, and therefore in all. These

numbers represent the *proportions* of weight in which the two bases, potassa and soda, enter into analogous combinations; 590 of potassa is *equivalent* to 391 of soda. These facts with regard to combination are still expressed by the above supposition of equal particles, assuming that the weights of a particle of potassa and of soda are in the proportion of 590 to 391.

But we pursue our analysis further. We find that potassa is a compound of a metallic base, potassium, and of oxygen, in the proportion of 490 to 100; we suppose, then, that the particle of potassa consists of a particle of potassium and a particle of oxygen, and these latter particles, since we see no present need to suppose them divided, potassium and oxygen being simple bodies, we may call *atoms*, and assume to be indivisible. And by supposing all simple bodies to consist of such atoms, and compounds to be formed by the union of two, or three, or more of such atoms, we explain the occurrence of definite and multiple proportions, and we construct the Atomic Theory.

2. *Hypothesis of Atoms*.—So far as the assumption of such atoms as we have spoken of serves to express those laws of chemical composition which we have referred to, it is a clear and useful generalization. But if the Atomic Theory be put forwards (and its author, Dr. Dalton, appears to have put it forwards with such an intention,) as asserting that chemical elements are really composed of atoms, that is, of such particles not further divisible, we cannot avoid remarking, that for such a conclusion, chemical research has not afforded, nor can afford, any satisfactory evidence whatever. The smallest observable quantities of ingredients, as well as the largest, combine according to the laws of proportions and equivalence which have been cited above. How are we to deduce from such facts any

inference with regard to the existence of certain smallest possible particles? The Theory, when dogmatically taught as a physical truth, asserts that all observable quantities of elements are composed of proportional numbers of particles which can no further be subdivided; but all which observation teaches us is, that *if* there be such particles, they are smaller than the smallest observable quantities. In chemical experiment, at least, there is not the slightest positive evidence for the existence of such atoms. The assumption of indivisible particles, smaller than the smallest observable, which combine, particle with particle, will explain the phenomena; but the assumption of particles bearing this proportion, but *not* possessing the property of indivisibility, will explain the phenomena at least equally well. The decision of the question, therefore, whether the Atomic Hypothesis be the proper way of conceiving the chemical combinations of substances, must depend, not upon chemical facts, but upon our conception of substance. In this sense the question is an ancient and curious controversy, and we shall hereafter have to make some remarks upon it.

3. *Chemical Difficulties of the Hypothesis.*—But before doing this, we may observe that there is no small difficulty in reconciling this hypothesis with the facts of chemistry. According to the theory, all salts, compounded of an acid and a base, are analogous in their atomic constitution; and the number of atoms in one such compound being known or assumed, the number of atoms in other salts may be determined. But when we proceed in this course of reasoning to other bodies, as metals, we find ourselves involved in difficulties. The protoxide of iron is a base which, according to all analogy, must consist of one atom of iron and one of oxygen: but the peroxide of iron is also a base, and it appears by the analysis of this substance that it must consist of *two*-

thirds of an atom of iron and one atom of oxygen. Here, then, our indivisible atoms must be divisible, even upon chemical grounds. And if we attempt to evade this difficulty by making the peroxide of iron consist of two atoms of iron and three of oxygen, we have to make a corresponding alteration in the theoretical constitution of all bodies analogous to the protoxide; and thus we overturn the very foundation of the theory. Chemical facts, therefore, not only do not prove the Atomic Theory as a physical truth, but they are not, according to any modification yet devised of the theory, reconcilable with its scheme.

Nearly the same conclusions result from the attempts to employ the Atomic Hypothesis in expressing another important chemical law;—the law of the combinations of gases according to definite proportions of their volumes, experimentally established by Guy Lussac*. In order to account for this law, it has been very plausibly suggested that all gases, under the same pressure, contain an equal number of atoms in the same space; and that when they combine, they unite atom to atom. Thus one volume of chlorine unites with one volume of hydrogen, and form hydrochloric acid†. But then this hydrochloric acid occupies the space of the two volumes; and therefore the proper number of particles cannot be supplied, and the uniform distribution of atoms in all gases maintained, without dividing into two each of the compound particles, constituted of an atom of chlorine and an atom of hydrogen. And thus in this case, also, the Atomic Theory becomes untenable if it be understood to imply the indivisibility of the atoms.

In all these attempts to obtain a distinct physical conception of chemical union by the aid of the Atomic Hypothesis, the atoms are conceived to be associated by

* *Hist. Ind. Sc.*, iii., 153.

† DUMAS, *Phil. Chim.* 263.

certain forces of the nature of mechanical attractions. But we have already seen* that no such mode of conception can at all explain or express the facts of chemical combination; and therefore it is not wonderful that when the Atomic Theory attempts to give an account of chemical relations by contemplating them under such an aspect, the facts on which it grounds itself should be found not to authorise its positive doctrines; and that when these doctrines are tried upon the general range of chemical observation, they should prove incapable of even expressing, without self-contradiction, the laws of phenomena.

4. *Grounds of the Atomic Doctrine.*—Yet the doctrine of atoms, or of substance as composed of indivisible particles, has in all ages had great hold upon the minds of physical speculators; nor would this doctrine ever have suggested itself so readily, or have been maintained so tenaciously, as the true mode of conceiving chemical combinations, if it had not been already familiar to the minds of those who endeavour to obtain a general view of the constitution of nature. The grounds of the assumption of the atomic structure of substance are to be found rather in the idea of substance itself, than in the experimental laws of chemical affinity. And the question of the existence of atoms, thus depending upon an idea which has been the subject of contemplation from the very infancy of philosophy, has been discussed in all ages with interest and ingenuity. On this very account it is unlikely that the question, so far as it bears upon chemistry, should admit of any clear and final solution. Still it will be instructive to look back at some of the opinions which have been delivered respecting this doctrine.

5. *Ancient Prevalence of the Atomic Doctrine.*—The doctrine that matter consists of minute, simple, indivisible,

* See Chapter I. of this Book.

indestructible particles as its ultimate elements, has been current in all ages and countries, whenever the tendency of man to wide and subtle speculations has been active. I need not attempt to trace the history of this opinion in the schools of Greece and Italy. It was the leading feature in the physical tenets of the Epicureans, and was adopted by their Roman disciples, as the poem of Lucretius copiously shows us. The same tenet had been held at still earlier periods, in forms more or less definite, by other philosophers. It is ascribed to Democritus, and is said to have been by him derived from Leucippus. But this doctrine is found also, we are told*, among the speculations of another intellectual and acute race, the Hindoos. According to some of their philosophical writers, the ultimate elements of matter are atoms, of which it is proved by certain reasonings, that they are each one-sixth of one of the motes that float in the sunbeam.

This early prevalence of controversies of the widest and deepest kind, which even in our day remain undecided, has in it nothing which need surprise us; or, at least, it has in it nothing which is not in conformity with the general course of the history of philosophy. As soon as any ideas are clearly possessed by the human mind, its activity and acuteness in reasoning upon them are such, that the fundamental antitheses and ultimate difficulties which belong to them are soon brought into view. The Greek and Indian philosophers had mastered completely the Idea of Space, and possessed the Idea of Substance in tolerable distinctness. They were, therefore, quite ready, with their lively and subtle minds, to discuss the question of the finite and infinite divisibility of matter, so far as it involved only the ideas of space and of sub-

* By Mr. Colebrook. *Asiatic Res.* 1824.

stance, and this accordingly they did with great ingenuity and perseverance.

But the ideas of Space and of Substance are far from being sufficient to enable men to form a complete general view of the constitution of matter. We must add to these ideas, that of mechanical Force with its antagonist Resistance, and that of the Affinity of one kind of matter for another. Now the former of these ideas the ancients possessed in a very obscure and confused manner; and of the latter they had no apprehension whatever. They made vague assumptions respecting the impact and pressure of atoms on each other; but of their mutual attraction and repulsion they never had any conception, except of the most dim and wavering kind; and of an affinity different from mere local union they did not even dream. Their speculations concerning atoms, therefore, can have no value for us, except as a part of the history of science. If their doctrines appear to us to approach near to the conclusions of our modern philosophy, it must be because our modern philosophy has not fully profited by the additional light which the experiments and meditations of later times have thrown upon the constitution of matter.

6. *Bacon*.—Still, when modern philosophers look upon the Atomic Theory of the ancients in a general point of view merely, without considering the special conditions which such a theory must fulfil, in order to represent the discoveries of modern times, they are disposed to regard it with admiration. Accordingly we find Francis Bacon strongly expressing such a feeling. The Atomic Theory is selected and dwelt upon by him as the chain which connects the best parts of the physical philosophy of the ancient and the modern world. Among his works is a remarkable dissertation *On the Philosophy of Democritus, Parmenides, and Telesius*: the last mentioned of whom was one of the revivers of physical science in modern times. In

this work he speaks of the atomic doctrine of Democritus as a favourable example of the exertions of the undisciplined intellect. "*Hæc ipsa placita, quamvis paulo emendatiora, talia sunt qualia esse possunt ille quæ ab intellectu sibi permissa, nec continenter et gradatim sublevato, profecta videntur.*"—"Accordingly," he adds, "the doctrine of Atoms, from its going a step beyond the period in which it was advanced, was ridiculed by the vulgar, and severely handled in the disputations of the learned, notwithstanding the profound acquaintance with physical science by which its author was allowed to be distinguished, and from which he acquired the character of a magician."

"However," he continues, "neither the hostility of Aristotle, with all his skill and vigour in disputation, (though, like the Ottoman sultans, he laboured to destroy all his brother philosophers that he might rest undisputed master of the throne of science,) nor the majestic and lofty authority of Plato, could effect the subversion of the doctrine of Democritus. And while the opinions of Plato and Aristotle were rehearsed with loud declamation and professorial pomp in the schools, this of Democritus was always held in high honour by those of a deeper wisdom, who followed in silence a severer path of contemplation. In the days of Roman speculation it kept its ground and its favour; Cicero everywhere speaks of its author with the greatest praise; and Juvenal, who, like poets in general, probably expressed the prevailing judgment of his time, proclaims his merit as a noble exception to the general stupidity of his countrymen.

. . . . Cujus prudentia monstrat
 Magnos posse viros et magna exempla daturus
 Vervecum in patriâ crassoque sub aere nasci.

"The destruction of this philosophy was not effected by Aristotle and Plato, but by Genseric and Attila, and

their barbarians. For then, when human knowledge had suffered shipwreck, those fragments of the Aristotelian and Platonic philosophy floated on the surface like things of some lighter and emptier sort, and so were preserved; while more solid matters went to the bottom, and were almost lost in oblivion."

7. *Modern Prevalence of the Atomic Doctrine.*—It is our business here to consider the doctrine of Atoms only in its bearing upon existing physical sciences, and I must therefore abstain from tracing the various manifestations of it in the schemes of hypothetical cosmologists;—its place among the *vortices* of Descartes, its exhibition in the *monads* of Leibnitz. I will, however, quote a passage from Newton to show the hold it had upon his mind.

At the close of his *Opticks* he says, "All these things being considered, it seems probable to me that God, in the beginning, formed matter in solid, massy, hard, impenetrable, moveable particles, of such sizes and figures, and with such other properties, and in such proportions to space, as most conduced to the end for which He formed them; and that these primitive particles, being solids, are incomparably harder than any porous bodies compounded of them, even so very hard as never to wear or break in pieces; no ordinary power being able to divide what God had made one in the first creation. While the particles continue entire, they may compose bodies of one and the same nature and texture in all ages: but should they wear away or break in pieces, the nature of things depending on them would be changed. Water and earth composed of old worn particles and fragments of particles would not be of the same nature and texture now with water and earth composed of entire particles in the beginning. And therefore that nature may be lasting, the changes of corporeal things are to be placed only in the various separations and new associa-

tions and motions of these permanent particles; compounded bodies being apt to break, not in the midst of solid particles, but where those particles are laid together and only touch in a few points."

We shall hereafter see how extensively the atomic doctrine has prevailed among still more recent philosophers. Not only have the chemists assumed it as the fittest form for exhibiting the principles of multiple proportions; but the physical mathematicians, as Laplace and Poisson, have made it the basis of their theories of heat, electricity, capillary action; and the crystallographers have been supposed to have established both the existence and the arrangement of such ultimate molecules.

In the way in which it has been employed by such writers, the hypothesis of ultimate particles has been of great use, and is undoubtedly permissible. But when we would assert this theory, not as a convenient hypothesis for the expression or calculation of the laws of nature, but as a philosophical truth respecting the constitution of the universe, we find ourselves checked by difficulties of reasoning which we cannot overcome, as well as by conflicting phenomena which we cannot reconcile. I will attempt to state briefly the opposing arguments on this question.

8. *Arguments for and against Atoms.*—The leading arguments on the two sides of the question, in their most general form, may be stated as follows:—

For the Atomic Doctrine.—The appearances which nature presents are compounded of many parts, but if we go on resolving the larger parts into smaller, and so on successively, we must at last come to something simple. For that which is compound can be so no otherwise than by composition of what is simple; and if we suppose all composition to be removed, which hypothetically we may do, there can remain nothing but a number of simple

substances, capable of composition, but themselves not compounded. That is, matter being dissolved, resolves itself into atoms.

Against the Atomic Doctrine.—Space is divisible without limit, as may be proved by geometry; and matter occupies space, therefore matter is divisible without limit, and no portion of matter is *indivisible*, or an *atom*.

And to the argument on the other side just stated, it is replied that we cannot even hypothetically divest a body of composition, if by composition we mean the relation of point to point in space. However small be a particle, it is compounded of parts having relation in space.

The Atomists urge again, that if matter be infinitely divisible, a finite body consists of an infinite number of parts, which is a contradiction. To this it is replied, that the finite body consists of an infinite number of parts in the same sense in which the parts are infinitely small, which is no contradiction.

But the opponents of the Atomists not only rebut, but retort this argument drawn from the notion of infinity. Your atoms, they say, are indivisible by any finite force; therefore they are infinitely hard; and thus your finite particles possess infinite properties. To this the Atomists are wont to reply, that they do not mean the hardness of their particles to be infinite, but only so great as to resist all usual natural forces. But here it is plain that their position becomes untenable; for, in the first place, their assumption of this precise degree of hardness in the particles is altogether gratuitous; and in the next place, if it were granted, such particles are not atoms, since in the next moment the forces of nature may be augmented so as to divide the particle, though hitherto undivided.

Such are the arguments for and against the Atomic Theory in its original form. But when these atoms are

conceived, as they have been by Newton, and commonly by his followers, to be solid, hard particles exerting attractive and repulsive forces, a new set of arguments come into play. Of these, the principal one may be thus stated: According to the Atomic Theory thus modified, the properties of bodies depend upon the attractions and repulsions of the particles. Therefore, among other properties of bodies, their hardness depends upon such forces. But if the hardness *of the bodies* depends upon the forces, the repulsion, for instance, of the particles, upon what does the hardness *of the particles* depend? what progress do we make in explaining the properties of bodies, when we assume the same properties in our explanation? and to what purpose do we assume that the particles *are* hard?

9. *Transition to Boscovich's Theory.*—To this difficulty it does not appear easy to offer any reply. But if the hardness and solidity of the particles be given up as an incongruous and untenable appendage to the Newtonian view of the Atomic Theory, we are led to the theory of Boscovich, according to which matter consists not of solid particles, but of mere mathematical centres of force. According to this theory, each body is composed of a number of geometrical points from which emanate forces, following certain mathematical laws in virtue of which they become, at certain small distances attractive, at certain other distances repulsive, and at greater distances attractive again. From these forces of the points arise the cohesion of the parts of the same body, the resistance which it exerts against the pressure of another body, and finally the attraction of gravitation which it exerts upon bodies at a distance.

This theory is at least a homogeneous and consistent mechanical theory, and it is probable that it may be used as an instrument for investigating and expressing true laws of nature; although, as we have already said, the

attempt to identify the forces by which the particles of bodies are bound together with mechanical attraction appears to be a confusion of two separate ideas.

10. *Use of the Molecular Hypothesis.*—In this form, representing matter as a collection of molecules or centres of force, the Atomic Theory has been abundantly employed in modern times as an hypothesis on which calculations respecting the elementary forces of bodies might be conducted. When thus employed it is to be considered as expressing the principle that the properties of bodies depend upon forces emanating from immovable points of their mass. This view of the way in which the properties of bodies are to be treated by the mechanical philosopher was introduced by Newton, and was a natural sequel to the success which he had obtained by reasoning concerning central forces on a large scale. I have already quoted his Preface to the *Principia*, in which he says, “Many things induce me to believe that the rest of the phenomena of nature, as well as those of astronomy, may depend upon certain forces by which the particles of bodies, in virtue of causes not yet known, are urged towards each other and cohere in regular figures, or are mutually repelled and recede; and philosophers, knowing nothing of these forces, have hitherto failed in their examination of nature.” Since the time of Newton, this line of speculation has been followed with great assiduity, and by some mathematicians with great success. In particular Laplace has shown that it may, in many instances, be made a much closer representation of nature, if we suppose the forces exerted by the particles to decrease so rapidly with the increasing distance from them, that the force is finite only at distances imperceptible to our senses, and vanishes at all remoter points. He has taught the method of expressing and calculating such forces, and he and other mathematicians of his

school have applied this method to many of the most important questions of physics; as capillary action, the elasticity of solids, the conduction and radiation of heat. The explanation of many apparently unconnected and curious observed facts by these mathematical theories gives us a strong assurance that its essential principles are true. But it must be observed that the actual constitution of bodies as composed of distinct and separate particles is by no means proved by these coincidences. The assumption, in the reasoning, of certain centres of force acting at a distance, is to be considered as nothing more than a method of reducing to calculation that view of the constitution of bodies, which supposes that they exert force at *every* point. It is a mathematical artifice of the same kind as the hypothetical division of a body into infinitesimal parts, in order to find its centre of gravity; and no more implies a physical reality than that hypothesis does.

11. *Poisson's Inference*.—When, therefore, M. Poisson, in his views of Capillary Action, treats this hypothetical distribution of centres of force as if it were a physical fact, and blames Laplace for not taking account of their different distribution at the surface of the fluid and below it*, he appears to push the claims of the molecular hypothesis too far. The only ground for the assumption of separate centres, is that we can thus explain the action of the whole mass. The intervals between the centres nowhere enter into this explanation: and therefore we can have no reason for assuming these intervals different in one part of the fluid and in the other. M Poisson asserts that the density of the fluid diminishes when we approach very near the surface; but he allows that this diminution is not detected by experiment, and that the formulæ on his supposition, so far as the results

* POISSON, *Theorie de l'Action Capillaire*.

go, are identical with those of Laplace. It is clear, then, that his doctrine consists merely in the assertion of the necessary truth of a part of the hypothesis which cannot be put to the test of experiment. It is true, that so long as we have before us the hypothesis of separate centres, the particles very near the surface are not in a condition symmetrical with that of the others: but it is also true that this hypothesis is only a step of calculation. There results, at one period of the process of deduction, a stratum of smaller density at the surface of the fluid; but at a succeeding point of the reasoning the thickness of this stratum vanishes; it has no physical existence.

Thus the *molecular* hypothesis, as used in such cases, does not differ from the doctrine of forces acting at *every point* of the mass; and this principle, which is common to both the opposite views, is the true part of each.

12. *Wollaston's Argument.*—An attempt has been made in another case, but depending on nearly the same arguments, to bring the doctrine of ultimate atoms to the test of observation. In the case of the air, we know that there *is* a diminution of density in approaching the upper surface of the atmosphere, if it have a surface: but it is held by some that except we allow the doctrine of ultimate molecules, it will not be bounded by any surface, but will extend to an infinite distance. This is the reasoning of Wollaston*. “If air consists of any ultimate particles no longer divisible, then must the expansion of the medium composed of them cease at that distance where the force of gravity downwards is equal to the resistance arising from the repulsive force of the medium.” But if there be no such ultimate particles, every stratum will require a stratum beyond it to prevent by its weight a further expansion, and thus the atmosphere must extend to an infinite distance. And Wollaston con-

* *Phil. Trans.*, 1822, p. 89.

ceived that he could learn from observation whether the atmosphere was thus diffused through all space; for if so, it must, he argued, be accumulated about the larger bodies of the system, as Jupiter and the Sun, by the law of universal gravitation; and the existence of an atmosphere about these bodies, might, he remarked, be detected by its effects in producing refraction. His result is, that "all the phenomena accord entirely with the supposition that the earth's atmosphere is of finite extent, limited by the weight of ultimate atoms of definite magnitude, no longer divisible by repulsion of their parts."

A very little reflection will show us that such a line of reasoning cannot lead to any result. For we know nothing of the law which connects the density with the compressing force, in air so extremely rare as we must suppose it to be near the boundary of the atmosphere. Now there are possible laws of dependence of the density upon the compressing force such that the atmosphere would terminate in virtue of the law without any assumption of atoms. This may be proved by mathematical reasoning. If we suppose the density of air to be as the square root of the compressing force, it will follow that at the very limits of the atmosphere, the strata of equal thickness may observe in their densities such a law of proportion as is expressed by the numbers 7, 5, 3, 1*.

If it be asked how, on this hypothesis, the density of the highest stratum can be as 1, since there is nothing to

* For the compressing force on each being as the whole weight beyond it, will be for the four highest strata, 16, 9, 4 and 1, of which the square roots are as 4, 3, 2, 1, or, as 8, 6, 4, 2; and though these numbers are not exactly as the densities 7, 5, 3, 1, those who are a little acquainted with mathematical reasoning, will see that the difference arises from taking so small a number of strata. If we were to make the strata indefinitely thin, as to avoid error we ought to do, the coincidence would be exact; and thus, according to this law, the series of strata terminates as we ascend, without any consideration of atoms.

compress it, we answer that the upper part of the highest stratum compresses the lower, and that the density diminishes continually to the surface, so that the need of compression and the compressing weight vanish together.

The fallacy of concluding that because the height of the atmosphere is finite, the weight of the highest stratum must be finite, is just the same as the fallacy of those who conclude that when we project a body vertically upwards, because it occupies only a finite time in ascending to the highest point, the velocity at the last instant of the ascent must be finite. For it might be said, if the last velocity of ascent be not finite, how can the body describe the last particle of space in a finite time? and the answer is, that there is no last finite particle of space, and therefore no last finite velocity.

13. *Permanence of Properties of Bodies.*—We have already seen that, in explaining the properties of matter as we find them in nature, the assumption of solid, hard, indestructible particles is of no use or value. But we may remark, before quitting the subject, that Newton appears to have had another reason for assuming such particles, and one well worthy of notice. He wished to express, by means of this hypothesis, the doctrine that the laws of nature do not alter with the course of time. This we have already seen in the quotation from Newton. "The ultimate particles of matter are indestructible, unalterable, impenetrable; for if they could break or wear, the structure of material bodies now would be different from that which it was when the particles were new." No philosopher will deny the truth which is thus conveyed by the assertion of atoms; but it is obviously equally easy for a person who rejects the atomic view, to state this truth by saying that the forces which matter exerts do not vary with time; but however modified by the new modifications of its form, are always unimpaired

in quantity, and capable of being restored to their former mode of action.

We now proceed to speculations in which the fundamental conceptions may, perhaps, be expressed, at least in some cases, by means of the arrangement of atoms ; but in which the philosophy of the subject appears to require a reference to a new Fundamental Idea.

LETTER VII.

Cause of definite proportions—Atomic Theory—Definition of Physical and Chemical Atoms, practically indivisible by mechanical and chemical means respectively. Compound Atoms or Molecules—Atomic Weights—Distinction between the facts and the hypothesis.

It is easy to understand that the question as to the why? as to the cause of these fixed invariable weights in chemical compounds, must necessarily have occupied the attention of chemists. There must certainly be *some cause* which renders impossible the combination of elements in any other than certain definite proportions, *something* which opposes an invincible obstacle to any diminution or augmentation of these relative proportions.

The fixed and invariable amounts of the combining proportions or equivalents of bodies are the manifestations of this hidden cause, but these manifestations form the limit of the domain of true experimental investigation; the cause itself is beyond our powers of perception,—our sphere of research,—and can only be a subject for the exercise of speculation—for the exercise of the reflective intellectual faculties.

In endeavouring to develope the theory which at present prevails, respecting the cause of the unchangeableness of chemical proportions, let it not be forgotten, that its truth or falsehood has nothing whatever to do with the natural law itself. The latter is the expression of universal experience; it remains true, invariably and immutably, however our notions respecting its cause may, from time to time, vary and change.

A very ancient opinion respecting the nature of matter, well known as the theory of atoms, is, in truth, exceedingly well adapted to render the law of definite proportions intelligible to our understanding.

The atomic theory supposes that the space occupied by a solid, fluid, or æriform body, is not in every part filled with matter; but that every such substance has pores, or interstices, between its particles of solid matter, which pores are not like those of a piece of wood, visible, but are of an infinitely smaller size. According to this view all bodies consist of exceedingly minute particles placed at a certain distance from each other, so that there exists between every two particles, or, rather, around every individual particle, a space not filled with the matter composing the substance itself.

It must be admitted that this view of the nature of matter is highly probable. We can compress a volume of air into a space a thousand times smaller than it originally occupied, and even fluid and solid substances are capable of being compressed, by mechanical pressure, into less space than they fill under ordinary circumstances. A billiard-ball thrown with considerable force upon a hard substance becomes flattened, and, after rebounding, resumes its spherical form. All bodies expand and fill a larger space when heated, and contract into a smaller space when exposed to a low temperature.

All these well-known facts manifestly prove that the space which a body occupies at any given time depends upon accidental circumstances; that this space varies by the operation of such causes as temperature and pressure, which tend to render it greater or smaller. Now, when we reflect that the place within any body, occupied by one of its smallest particles, cannot at the same time be occupied by a second and a third particle, we cannot help drawing the conclusion that the augmentation or diminution of its volume, which we have described, is a consequence of a greater or less distance between its space-filling particles. Thus, in a pound of liquid water, the particles of the water must evidently be nearer to each other than they are in a pound of steam, which occupies a space 1700 times greater than a pound of liquid water.

This theory affords us an intelligible insight into a number

of phenomena, which, although simple in themselves, have hitherto been altogether inexplicable upon any other supposition.

Again, the atomic theory presupposes that the small particles composing the mass of any substance are incapable of further division,—that they are indivisible particles or *atoms*, a term applied to the ultimate particles of bodies, derived from the Greek, *α*, *not*, and *τεμνω*, *to cut*.

It is impossible for the human mind to imagine particles of matter to be absolutely indivisible, since they cannot be infinitely small in a mathematical sense, that is to say, altogether without extension, because they possess a certain weight; and how minute soever we may assume this weight to be, yet we cannot consider the division of a particle possessing weight to be impossible into two, three, nay into a hundred parts. But we may also suppose that the ultimate atoms of bodies are only physically indivisible; they are only incapable of further subdivision so far as our powers of perception enable us to judge.

A physical *atom* in this sense, then, is a conglomeration of innumerable smaller imaginary particles, held together by a force or forces more powerful than all the means at our command for their further subdivision or dissolution.

The term *atom* is employed by chemists in a sense precisely analogous to that attached by them to the word *element*.

The sixty-one substances at present known and supposed to be simple bodies or elements are so considered, not absolutely, but only relatively to our powers, because we are not able by any means we possess at present to decompose them,—that is, to separate them into still more simple elements; and, adhering to the true principles of natural philosophy, we call them simple bodies or elements, until experience shall demonstrate them to be compound.

The history of science presents us with abundant illustrations of the supreme importance of a strict adherence to this rule of philosophical inquiry,—retrogression, errors, and

fallacious theories innumerable, having invariably followed the transgression of the limits of experience.

Without disputing the infinite divisibility of matter, the chemist merely maintains the firm and immovable foundation of his science, when he admits the existence of physical ATOMS as a truth, entirely incontrovertible.

A professor of Tübingen (Gmelin) has endeavoured, by an ingenious illustration, to render the atomic theory of chemists more intelligible. He compares atoms to the heavenly bodies, which, in comparison with the extent of the space in which they are suspended, are infinitely small, that is, are *atoms*. Innumerable suns, with their planets and attendant satellites, move in infinite space, at definite and measured distances from each other; they are individually indivisible, inasmuch as there exists no force capable of separating them into parts, tearing off from them anything material, or altering their size or form in such a degree as to be perceptible, or to impair or disturb their relations to the other heavenly bodies, but they are not indivisible *per se*.

In this sense the whole universe coalesces into one immense body, the atoms of which—that is, suns, planets, and satellites—are indivisible and unchangeable!

According to the atomic theory, then, a piece of glass, of cinnabar, of iron, &c., is a heap or congeries of atoms of glass, cinnabar, iron, &c., the connection of which, in masses, depends upon the power or attraction of cohesion. The smallest particle we can imagine of the iron is still *iron*. But we know, with positive certainty, with respect to the cinnabar, that its smallest particle, although physically indivisible, is made up of still smaller particles; that is, that it must contain particles of sulphur and particles of mercury; and we further know even the relative proportions, by weight, of these two substances contained in the physically indivisible particle of cinnabar.

The iron consists of homogeneous atoms of iron; the cinnabar also consists of homogeneous atoms, each of which is cinnabar; but these latter atoms are not simple, like those of the iron, but they are capable of being separated into

constituent parts : they are homogeneous as far as our senses reach, but we nevertheless know their nature to be compound. We may, by the mere mechanical processes of filing, trituration, &c., reduce a piece of cinnabar into an innumerable quantity of small particles, but no merely mechanical force will enable us to overcome that power by which the heterogeneous particles forming the constituents of a complex atom like that of cinnabar are kept united.

It is precisely in this that chemical affinity differs from the power of cohesion, or cohesive attraction, as it is called,—that it becomes active and manifest only when *dissimilar* atoms are brought into contact with each other ; and since it is impossible that atoms should penetrate and become mutually diffused throughout each other, it follows that such compound atoms must be formed by the aggregation, or grouping side by side, of the simple atoms, in consequence of the power of affinity acting so as to associate them into compound atoms,—one atom of one simple body being aggregated with one, two, three, or more atoms of another body, and so on,—every such group being a part exactly analogous to the mass of a substance perceptible to our senses. Thus, we may suppose the very smallest particle of cinnabar we can imagine, consists of a group of two atoms, namely, one atom of mercury, and one atom of sulphur.

When we consider that a thousand pounds weight of cinnabar contains exactly the same relative proportions of mercury and of sulphur as a single pound, or a single grain,—and although a piece of cinnabar large enough to be manifest to our senses must contain, perhaps, millions of *atoms* of cinnabar,—yet it must be evident that in every single atom, equally as in the mass made up of millions of atoms, 100 parts by weight of mercury are invariably united to 16 of sulphur. If we decompose cinnabar by means of iron, the atom of mercury is displaced, and an atom of iron is substituted for it. Or if we replace the sulphur of the cinnabar by oxygen, one atom of oxygen takes the place of the atom of sulphur.

You will now perceive that, according to this theory of the

constitution of bodies, and their mutual substitution in combinations, the numbers denominated equivalents express nothing else than the relative weight of the atoms. The *absolute* weight of a single atom of any substance is not within the reach of our faculties to determine ; but how much more or less weight one body brings into a combination than another, that is to say, the *relative* weight of atoms, can readily be ascertained.

Since to replace 8 parts by weight of oxygen 16 parts by weight of sulphur are required, that is, double the weight of the oxygen, the atom of sulphur is twice as heavy as that of oxygen.

In substituting hydrogen for oxygen in any compound, only one-eighth part of the weight of the latter substance is required to one part of the former ; it is evident that the weight of the atom of hydrogen is eight times lighter than the atom of oxygen. Carbonic oxide is a group of *two* atoms, containing one atom of carbon and one atom of oxygen. Carbonic acid is a group of *three* atoms, containing two atoms of oxygen to one of carbon.

The immutability of the proportions, by weight, in which bodies combine, is fully explained theoretically by thus assuming the existence of indivisible ultimate particles, which are of unequal weights, incapable of penetrating or being diffused through each other when they are united in chemical combination, but being arranged together side by side.

The real experimental import of the equivalent numbers is the expression of the proportional and relative weight of bodies in which they produce equivalent effects in chemical combinations ; and these effects we represent to our minds, and render intelligible, by ascribing them to indivisible particles, or *atoms*, which occupy a certain space, and possess a certain form, or shape. We possess no means of ascertaining the *number* of atoms, even in the most simple compound, since for this purpose it would be necessary that we should be able to see and to count them, and therefore, notwithstanding our firm conviction of the existence of physical

atoms, the supposition that the equivalent numbers actually express the relative weights of the individual atoms, is only an hypothesis, for which we have no further proofs.

One atom of cinnabar contains 16 of sulphur to 100 of mercury; now chemists, in assuming that these proportions express the relative weight of *one atom* of mercury and *one atom* of sulphur, pass from experimental certainty into hypothesis; for this mode of representation is merely hypothetical. 100 of mercury may, for aught we know to the contrary, represent the weight of two, three, four, or more *atoms*. Should it represent two atoms, one atom of mercury would be expressed by 50; should it represent three atoms, one atom would be expressed by 33.3. In the first case cinnabar would consist of two atoms, twice 50, in the latter case of three atoms, thrice 33.3 of mercury, to one atom of sulphur.

Whatever supposition we may entertain in this respect, whether we assume the composition of cinnabar to require two, three, or more atoms of mercury or sulphur, its constitution remains invariably the same. It is only the method by which we represent the composition of a chemical compound to our minds, which would vary with the hypothetical view respecting the number of atoms contained in the compound. It will, therefore, always be most advisable to banish all that is hypothetical from the symbolic language of chemistry, more especially as the only purpose of this language is to demonstrate to our sense of sight, and to render easy of apprehension, the composition of chemical compounds. The method of representing the constitution of compound substances ought never to be used for expressing unsettled and mutable notions or speculative theories. The number of the equivalents of the constituents of a chemical compound is invariable, and strictly definable, but the number of atoms necessary to make up an equivalent will never be ascertained. There is not, however, the slightest disadvantage in assuming that the equivalents represent the weights of the atoms themselves in cases where theoretical considerations, the mere explanation of ideas, is concerned. In this sense those numbers express merely the

difference between the weights of various atoms ; that is, by how much the weight of the atom of one body is heavier than that of another.

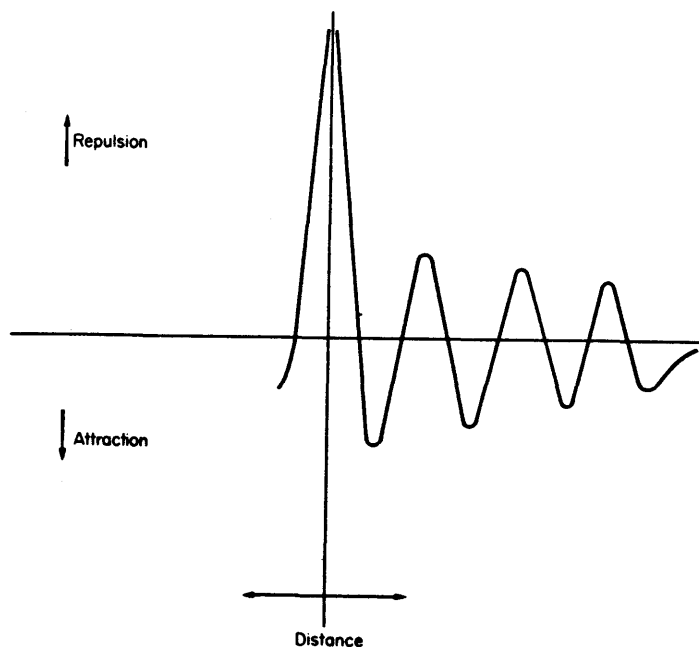
The numbers in the table given at p. 96 refer to the relative weights required to replace 1 part by weight of hydrogen, or to the replacement of the weight of oxygen which, in water, is combined with 1 part of hydrogen. Water contains 8 parts by weight of oxygen, to 1 part by weight of hydrogen. Upon the supposition, then, that water consists of a single atom of oxygen, combined with a single atom of hydrogen,—and, on the further supposition that the replacement of one atom of hydrogen, or one atom of oxygen, invariably requires one atom of any other body, and neither more nor less,—then these equivalent weights of all other bodies express their atomic weights, and the numbers by which they are represented all refer to the assumed unit, to 1 part by weight of hydrogen, or 8 parts by weight of oxygen.

If we multiply all these equivalent numbers by 12·5, we obtain the equivalent numbers, 12·5 for hydrogen and 100 for oxygen ; and the other numbers express, then, the amount of each substance which is required to replace 100 of oxygen or 12·5 of hydrogen. The multiplication of the equivalents by one and the same number does not, of course, alter their relative proportions, and it is, therefore, quite immaterial whether we use numbers referring to hydrogen as a unit, or to oxygen as 100.

Section III

THE BOSCOVICH ATOM AND THE THEORY OF MATTER

Roger Joseph Boscovich wished to escape from the crudities of the billiard ball atom, and proposed instead that atoms be considered as mere mathematical points, or centres of force, endowed with inertia. He illustrated his ideas with a diagram:



The repulsive force between two point atoms rises to infinity as they are pushed closer together. At great distances the forces are attractive, and correspond to gravitation. Other troughs on the graph correspond to stable interatomic distances, in solids, liquids, and chemical compounds. The advantage of Boscovich's theory was that minimal properties were assigned to the actual atom; one could hardly

demand a simpler model than a mathematical point. The disadvantage was that it seemed highly abstruse; a world of Boscovich atoms might well be suspected to be no more than a pale shadow of the real world.

Boscovich's theory did not attract great attention on the Continent, but in England it gained a number of adherents, of whom the most notable were Joseph Priestley, Davy, Michael Faraday, and—at various times—Lord Kelvin. Davy liked the theory because of its simplicity, and in a dialogue unfinished at his death and not published until eleven years later, he sought to show how the theory might be applied in chemistry. One of the attractions of the theory was that it seemed possible to reconcile the Kantian view of chemical combination as a true synthesis, and not merely a juxtaposition of particles, with a view of matter as composed of point atoms. This appealed to Faraday, who also showed that it was impossible to avoid the absurd conclusion that empty space was sometimes a conductor of electricity, and sometimes an insulator, if one subscribed to the Daltonian view, that matter was composed of solid atoms with space between them.

In later discussions Faraday's authority was often claimed for the doctrine of the unity of matter, a doctrine which he had derived from Davy. Davy's suggestion of 1812 that hydrogen might be present in all inflammable bodies was a survival of the phlogiston theory, as was the notion that water might be the ponderable matter of oxygen and hydrogen. The idea that 'ammonium' might be the type of all the metals arose from Davy's studies of sodium and potassium, which he had discovered. The oddest suggestion is that chlorine might be an oxide; for one of Davy's great achievements had been to establish that no experiments had so far shown that chlorine could be decomposed, and so it should be regarded as an element. Davy insisted on the simplicity and harmony of nature, and desired to see the number of elements reduced; but he was able to keep fact and theory separate in this rather odd way.

Over half a century later Dumas took up this question. Where Davy had compared 'ammonium' to the metals, Dumas pointed to the radicals of organic chemistry, groups which persisted through a series of reactions like elements do. Dumas and Liebig had in 1837 announced the 'radical theory'; that units like benzoyl ($\text{C}_6\text{H}_5\text{CO}$ —) were the elements of organic chemistry. Since these radicals behaved like elements, but could be decomposed, it seemed reasonable to suppose that the elements were really radicals too, which had so far resisted decomposition. Further, the radicals could be arranged in series, like methyl, ethyl, propyl; and Ostwald suggested in 1904 (see Section VI) that Dumas's remarks had been an important factor in leading to the arrangement of the elements in families in the Periodic Table of Mendeléeff.

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DIALOGUE THE SEVENTH.

ON THE CHEMICAL ELEMENTS.*

SCENE—THE APENNINES ABOVE PERUGIA.

PHIL.—Notwithstanding the magnificence of the Alpine country and the beauty of the upper part of Italy, yet the scenery now before us has peculiar charms, dependent not only upon the variety and grandeur of the objects which it displays, but likewise upon its historical relations. The hills are all celebrated in the early history of Italy, and many of them are crowned by Etruscan towns. The lake of Thrasimene spreads its broad and calm mirror beneath a range of hills covered

* [The Dialogue of which this fragment was the commencement, according to the original plan of the author, was intended to have followed one on the doctrine of definite proportions, which was partly written, and from which an extract has been given in the fifth volume. For the sake of uniformity, the designations of the speakers, as used in the preceding pages, have been continued: in the original, others were employed; the Unknown stands for Philo-chemicus, and Philaletes for Poietes.]

with oak and chesnut; and the eminence where Hannibal marshalled that army which had nearly deprived Rome of empire, is now of a beautiful green from the rising corn. Here the Tiber runs a clear and bright blue mountain stream, meriting the epithet of *ceruleus* bestowed upon it by Virgil; and there the Chiusan marsh sends its tributary streams from the same level to the rivers of Etruria and Latium. In the extreme distance are the woods of the Sabine country, bright with the purple foliage of the Judah tree, extending along the sides of blue hills, which again are capped by snowy mountains. How rich and noble is the scene! How vast its extent! How diversified its colours!

EUB.—The profusion of the rich tree, which renders the woods of so bright a colour, perhaps gave origin to the expression *ver purpureum*.

THE UNKNOWN.—The epithet purple will apply with equal justice to the woods of Sabina and the plains of Umbria, where the sainfoin gives the predominating tint, and it is now in full and luxuriant blossom, and the banks of the Clitumnus are, as it were, lighted up by this brilliant colour.

EUB.—Nature in this view is probably nearly the same as it was 2000 years ago; but *how man is changed!*—improved in civilization, but enfeebled in character. How unlike the ancient Umbrians and Sabines are the people who inhabit these mountains and valleys!

THE UNKNOWN. — The reason is obvious enough. Man is formed by his institutions; and moral and political causes almost create his character; whereas *nature* is governed by fixed laws. The atmosphere, the mountains, the valleys, the plains, the degrees of heat and cold, with small differences, have continued the same;

and whether peopled or deserted, the soil will always produce fruits or flowers, wild or cultivated.

PHIL.—If the exterior of the globe is liable to small changes only, there must be a permanency in the elements of things; something must be unalterable. Will you give us some ideas respecting this part of your philosophy,—which are the true elements of things? If there be a permanency or constancy in the arrangements of nature, matter cannot be infinite either in its divisibility or changes: pray give us some light on these obscure and difficult matters.

THE UNKNOWN.—I shall willingly enter upon this subject. I cannot demonstrate to you what are the true elements of things; but I can exhibit to you those substances, which, as we cannot decompose them, are elementary for us: mathematically considered, it appears possible to prove the infinite divisibility of matter; but our mechanical means of division are extremely limited. There is every reason to believe that our powers of chemical decomposition are far from having reached their *ultimatum*; yet in the operations of nature, as well as in those of art, certain substances appear to be unchangeable; thus, if we take a metal, such as iron, and dissolve it in an acid, or sublime it in union with an elastic fluid, or make it enter into a hundred combinations, it may still be recovered unaltered in its properties, the same in substance and in quantity. The test of a body being indecomposable is, that in all chemical changes it increases in weight, or its changes result from its combining with new matter. Thus when mercury is converted into a red powder by being heated in the air, it gains in weight. The test of a body being compound is, that in assuming new forms it loses weight; thus, when the olive-coloured substance called oxide of silver is

converted into silver by heat, it weighs less than before ; but in all cases, either of gain or loss of weight, the circumstance depends either upon matter absorbed, or matter emitted, which is either solid, fluid, or æriform, and which can be always collected and weighed. The metals, sulphur, phosphorus, carbon, silenium, iodine, brome, and certain elastic fluids are the only substances as far as our knowledge extends, which can be neither produced from other forms of matter, nor be converted into them. I explained to you on a former occasion that each of these substances enters into combinations in the same relative proportions, or in some multiple of those proportions ; and hence the idea has been entertained that they are minute indestructible particles, having always the same figure and weight. The weights of the smallest known relative proportions of the undecomposable bodies are these:—Hydrogen 1 ; chlorine 35·42 ; oxygen 8 ; fluorine 18·68 ; iodine 126·3 ; bromine 78·4 ; azote 14·15 ; sulphur 16·1 ; phosphorus 15·7 ; carbon 6·12 ; boron 10·9 ; selenium 39·6 ; silicium 7·5 ; aluminum 13·7 ; glucinum 17·7 ; ittrium 32·2 ; magnesium 12·7 ; zirconium 33·7 ; thorium 59·6 ; potassium 39·15 ; sodium 23·3 ; lithium 10 ; strontium 43·8 ; barium 68·7 ; calcium 20·5 ; manganese 27·7 ; zinc 32·3 ; iron 28 ; tin 58·9 ; arsenic 37·7 ; molybdenum 47·96 ; chromium 28 ; tungsten 94·8 ; columbium 185 ; antimony 64·6 ; uranium 217 ; cerium 46 ; cobalt 29·5 ; titanium 24·3 ; bismuth 71 ; copper 31·6 ; tellurium 32·3 ; cadmium 55·8 ; nickel 29·5 ; lead 103·6 ; mercury 202 ; osmium 99·7 ; silver 108 ; palladium 53·3 ; rhodium 52·2 ; gold 199·2 ; iridium 98·8 ; platinum 98·8.*

[* These numbers are taken from the table of equivalents of elementary substances formed by the late Dr Turner, and inserted in his

PHIL.—What is your idea of the cause of this difference of weight? Do you suppose their particles likewise of different sizes, or that they are of the same size, and have a different quantity of pores, or that their figures are different?

THE UNKNOWN. — These questions cannot be answered except by conjectures. At some time possibly we may be able to solve them by an hypothesis which will satisfactorily explain the chemical phenomena; but as we can never see the elementary particles of bodies, our reasoning upon them must be founded upon analogies derived from mechanics, and the idea that small indivisible particles follow the same laws of motion as the masses which they compose.

EUB.—I think it is contrary to the principles of sound philosophy to reason in this way. In mathematics it is always supposed that lines are composed from points, surfaces from lines, solids from surfaces; yet the elements bear no relation to their compounds. Again in light: according to your principle, white light would be composed of many particles of white light; whereas analysis proves it to be composed of various coloured particles, each differing from the other. On the hypothesis of Boscovitch, which is well explained in the *Institutio Physica* of Mako, matter, as well as I recollect, is supposed to be composed of indivisible points endowed with attraction and repulsion, which are assumed to be both physical and chemical elements.

Elements of Chemistry, the edition of 1834. The numbers 8 and 35.42 are given for oxygen and chlorine respectively, on the supposition, that water, and muriatic acid gas is each composed of one proportion of the constituent elements: should the view of the author be preferred, who, in his Elements of Chemical Philosophy, considered water as consisting of two proportions of hydrogen to one of oxygen and muriatic acid gas similarly constituted, all that is necessary is to multiply 8 and 35.42 by 2, and the numbers of all the other bodies accordingly.]

THE UNKNOWN.—You mistake me if you suppose I have adopted a system like the *Homooia* of Anaxagoras, and that I suppose the elements to be physical molecules endowed with the properties of the bodies we believe to be indecomposable. On the contrary, I neither suppose in them figure nor colour,—both would imply a power of reflecting light: I consider them, with Boscovitch, merely as points possessing weight and attractive and repulsive powers; and composing according to the circumstances of their arrangements either spherules or regular solids, and capable of assuming either one form or the other. All that is necessary for the doctrines of the corpuscular philosophy is to suppose the molecules which we are not able to decompose, spherical molecules; and that by the arrangement of spherical molecules regular solids are formed; and that the molecules have certain attractive and repulsive powers which correspond to negative and positive electricity. This is not mere supposition unsupported by experiments; there are various facts which give probability to the idea, which I shall now state to you. The *first fact* is, that all bodies are capable of being rendered fluid by a certain degree of heat, which supposes a freedom of motion in their particles that cannot be well explained except by supposing them spherical in the fluid state. The *second fact* is, that all bodies in becoming solid are capable of assuming regular polyhedral forms. The *third fact* is that all crystalline bodies present regular electrical poles. And the *fourth* is, that the elements of bodies are capable of being separated from each other by certain electrical attractions and repulsions.

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XXIII. *A speculation touching Electric Conduction and the Nature of Matter.* By MICHAEL FARADAY, Esq., D.C.L., F.R.S.

To Richard Taylor, Esq.

DEAR SIR,

Royal Institution, January 25, 1844.

LAST Friday I opened the weekly evening-meetings here by a subject of which the above was the title, and had no intention of publishing the matter further, but as it involves the consideration and application of a few of those main elements of natural knowledge, facts, I thought an account of its nature and intention might not be unacceptable to you, and would at the same time serve as the record of my opinion and views, as far as they are at present formed.

The view of the atomic constitution of matter which I think is most prevalent, is that which considers the atom as a something material having a certain volume, upon which those powers were impressed at the creation, which have given it, from that time to the present, the capability of constituting, when many atoms are congregated together into groups, the different substances whose effects and properties we observe. These, though grouped and held together by their powers, do not touch each other, but have intervening space, otherwise pressure or cold could not make a body contract into a smaller bulk, nor heat or tension make it larger; in liquids these atoms or particles are free to move about one another, and in vapours or gases they are also present, but removed very much further apart, though still related to each other by their powers.

The atomic doctrine is greatly used one way or another in this, our day, for the interpretation of phænomena, especially those of crystallography and chemistry, and is not so carefully distinguished from the facts, but that it often appears to him who stands in the position of student, as a statement of the facts themselves, though it is at best but an assumption; of the truth of which we can assert nothing, whatever we may say or think of its probability. The word atom, which can never be used without involving much that is purely hypothetical, is often *intended* to be used to express a simple fact, but, good as the intention is, I have not yet found a mind that did habitually separate it from its accompanying temptations; and there can be no doubt that the words definite proportions, equivalents, primes, &c., which did and do express fully all the *facts* of what is usually called the atomic theory in chemistry, were dismissed because they were not expressive enough, and did not say all that was in the mind of him who

used the word atom in their stead; they did not express the hypothesis as well as the fact.

But it is always safe and philosophic to distinguish, as much as is in our power, fact from theory; the experience of past ages is sufficient to show us the wisdom of such a course; and considering the constant tendency of the mind to rest on an assumption, and, when it answers every present purpose, to forget that it is an assumption, we ought to remember that it, in such cases, becomes a prejudice, and inevitably interferes, more or less, with a clear-sighted judgement. I cannot doubt but that he who, as a mere philosopher, has most power of penetrating the secrets of nature, and guessing by hypothesis at her mode of working, will also be most careful, for his own safe progress and that of others, to distinguish that knowledge which consists of assumption, by which I mean theory and hypothesis, from that which is the knowledge of facts and laws; never raising the former to the dignity or authority of the latter, nor confusing the latter more than is inevitable with the former.

Light and electricity are two great and searching investigators of the molecular structure of bodies, and it was whilst considering the probable nature of conduction and insulation in bodies not decomposable by the electricity to which they were subject, and the relation of electricity to space contemplated as void of that which by the atomists is called matter, that considerations something like those which follow were presented to my mind.

If the view of the constitution of matter already referred to be assumed to be correct, and I may be allowed to speak of the particles of matter and of the space between them (in water, or in the vapour of water for instance) as two different things, then space must be taken as the only continuous part, for the particles are considered as separated by space from each other. Space will permeate all masses of matter in every direction like a net, except that in place of meshes it will form cells, isolating each atom from its neighbours, and itself only being continuous.

Then take the case of a piece of shell-lac, a non-conductor, and it would appear at once from such a view of its atomic constitution that space is an insulator, for if it were a conductor the shell-lac could not insulate, whatever might be the relation as to conducting power of its material atoms; the space would be like a fine metallic web penetrating it in every direction, just as we may imagine of a heap of siliceous sand having all its pores filled with water; or as we may consider of a stick of black wax, which, though it contains an infinity of particles of conducting charcoal diffused through every

part of it, cannot conduct, because a non-conducting body (a resin) intervenes and separates them one from another, like the supposed space in the lac.

Next take the case of a metal, platinum or potassium, constituted, according to the atomic theory, in the same manner. The metal is a conductor; but how can this be, except space be a conductor? for it is the only continuous part of the metal, and the atoms not only do not touch (by the theory), but as we shall see presently, must be assumed to be a considerable way apart. Space therefore must be a conductor, or else the metals could not conduct, but would be in the situation of the black sealing-wax referred to a little while ago.

But if space be a conductor, how then can shell-lac, sulphur, &c. insulate? for space permeates them in every direction. Or if space be an insulator, how can a metal or other similar body conduct?

It would seem, therefore, that in accepting the ordinary atomic theory, space may be proved to be a non-conductor in non-conducting bodies, and a conductor in conducting bodies, but the reasoning ends in this, a subversion of that theory altogether; for if space be an insulator it cannot exist in conducting bodies, and if it be a conductor it cannot exist in insulating bodies. Any ground of reasoning which tends to such conclusions as these must in itself be false.

In connexion with such conclusions we may consider shortly what are the probabilities that present themselves to the mind, if the extension of the atomic theory which chemists have imagined, be applied in conjunction with the conducting powers of metals. If the specific gravity of the metals be divided by the atomic numbers, it gives us the number of atoms, upon the hypothesis, in equal bulks of the metals. In the following table the first column of figures expresses nearly the number of atoms in, and the second column of figures the conducting power of, equal volumes of the metals named.

Atoms.	Conducting power.
1.00 gold	6.00
1.00 silver	4.66
1.12 lead	0.52
1.30 tin	1.00
2.20 platinum ...	1.04
2.27 zinc	1.80
2.87 copper	6.33
2.90 iron	1.00

So here iron, which contains the greatest number of atoms in a given bulk, is the worst conductor excepting one. Gold, which contains the fewest, is nearly the best conductor; not

that these conditions are in inverse proportions, for copper, which contains nearly as many atoms as iron, conducts better still than gold, and with above six times the power of iron. Lead, which contains more atoms than gold, has only about one-twelfth of its conducting power; lead, which is much heavier than tin and much lighter than platina, has only half the conducting power of either of these metals. And all this happens amongst substances which we are bound to consider, at present, as elementary or simple. Whichever way we consider the particles of matter and the space between them, and examine the assumed constitution of matter by this table, the results are full of perplexity.

Now let us take the case of potassium, a compact metallic substance with excellent conducting powers, its oxide or hydrate a non-conductor; it will supply us with some facts having very important bearings on the assumed atomic construction of matter.

When potassium is oxidized an atom of it combines with an atom of oxygen to form an atom of potassa, and an atom of potassa combines with an atom of water, consisting of two atoms of oxygen and hydrogen, to form an atom of hydrate of potassa, so that an atom of hydrate of potassa contains four elementary atoms. The specific gravity of potassium is 0.865, and its atomic weight 40; the specific gravity of cast hydrate of potassa, in such state of purity as I could obtain it, I found to be nearly 2, its atomic weight 57. From these, which may be taken as facts, the following strange conclusions flow. A piece of potassium contains less potassium than an equal piece of the potash formed by it and oxygen. We may cast into potassium oxygen atom for atom, and then again both oxygen and hydrogen in a twofold number of atoms, and yet, with all these additions, the matter shall become less and less, until it is not two-thirds of its original volume. If a given bulk of potassium contains 45 atoms, the same bulk of hydrate of potassa contains 70 atoms nearly *of the metal potassium*, and besides that, 210 atoms more of oxygen and hydrogen. In dealing with assumptions I must assume a little more for the sake of making any kind of statement; let me therefore assume that in the hydrate of potassa the atoms are all of one size and nearly touching each other, and that in a cubic inch of that substance there are 2800 elementary atoms of potassium, oxygen and hydrogen; take away 2100 atoms of oxygen and hydrogen, and the 700 atoms of potassium remaining will swell into more than a cubic inch and a half, and if we diminish the number until only those containable in a cubic inch remain, we shall have 430, or thereabout.

So a space which can contain 2800 atoms, and amongst them 700 of potassium itself, is found to be entirely filled by 430 atoms of potassium as they exist in the ordinary state of that metal. Surely then, under the suppositions of the atomic theory, the atoms of potassium must be very far apart in the metal, *i. e.* there must be much more of space than of matter in that body: yet it is an excellent conductor, and so space must be a conductor; but then what becomes of shell-lac, sulphur, and all the insulators? for space must also by the theory exist in them.

Again, the volume which will contain 430 atoms of potassium, and nothing else, whilst in the state of metal, will, when that potassium is converted into nitre, contain very nearly the same number of atoms of potassium, *i. e.* 416, and also then seven times as many, or 2912 atoms of nitrogen and oxygen besides. In carbonate of potassa the space which will contain only the 430 atoms of potassium as metal, being entirely filled by it, will, after the conversion, contain 256 atoms more of potassium, making 686 atoms of that metal, and, in addition, 2744 atoms of oxygen and carbon.

These and similar considerations might be extended through compounds of sodium and other bodies with results equally striking, and indeed still more so, when the relations of one substance, as oxygen or sulphur, with different bodies are brought into comparison.

I am not ignorant that the mind is most powerfully drawn by the phenomena of crystallization, chemistry and physics generally, to the acknowledgement of centres of force. I feel myself constrained, for the present hypothetically, to admit them, and cannot do without them, but I feel great difficulty in the conception of atoms of matter which in solids, fluids and vapours are supposed to be more or less apart from each other, with intervening space not occupied by atoms, and perceive great contradictions in the conclusions which flow from such a view.

If we must assume at all, as indeed in a branch of knowledge like the present we can hardly help it, then the safest course appears to be to assume as little as possible, and in that respect the atoms of Boscovich appear to me to have a great advantage over the more usual notion. His atoms, if I understand aright, are mere centres of forces or powers, not particles of matter, in which the powers themselves reside. If, in the ordinary view of atoms, we call the particle of matter away from the powers *a*, and the system of powers or forces in and around it *m*, then in Boscovich's theory *a* disappears, or is a mere mathematical point, whilst in the usual notion it is

a little unchangeable, impenetrable piece of matter, and m is an atmosphere of force grouped around it.

In many of the hypothetical uses made of atoms, as in crystallography, chemistry, magnetism, &c., this difference in the assumption makes little or no alteration in the results, but in other cases, as of electric conduction, the nature of light, the manner in which bodies combine to produce compounds, the effects of forces, as heat or electricity, upon matter, the difference will be very great.

Thus, referring back to potassium, in which as a metal the atoms must, as we have seen, be, according to the usual view, very far apart from each other, how can we for a moment imagine that its conducting property belongs to it, any other-wise than as a consequence of the properties of the space, or as I have called it above, the m ? so also its other properties in regard to light or magnetism, or solidity, or hardness, or specific gravity, must belong to it, in consequence of the properties or forces of the m , not those of the a , which, without the forces, is conceived of as having no powers. But then surely the m is the *matter* of the potassium, for where is there the least ground (except in a gratuitous assumption) for imagining a difference in kind between the nature of that space midway between the centres of two contiguous atoms and any other spot between these centres? a difference in degree, or even in the nature of the power consistent with the law of continuity, I can admit, but the difference between a supposed little hard particle and the powers around it I cannot imagine.

To my mind, therefore, the a or nucleus vanishes, and the substance consists of the powers or m ; and indeed what notion can we form of the nucleus independent of its powers? all our perception and knowledge of the atom, and even our fancy, is limited to ideas of its powers: what thought remains on which to hang the imagination of an a independent of the acknowledged forces? A mind just entering on the subject may consider it difficult to think of the powers of matter independent of a separate something to be called *the matter*, but it is certainly far more difficult, and indeed impossible, to think of or imagine that *matter* independent of the powers. Now the powers we know and recognize in every phænomena of the creation, the abstract matter in none; why then assume the existence of that of which we are ignorant, which we cannot conceive, and for which there is no philosophical necessity?

Before concluding these speculations I will refer to a few of the important differences between the assumption of atoms consisting merely of centres of force, like those of Boscovich, and that other assumption of molecules of something specially material, having powers attached in and around them.

With the latter atoms a mass of matter consists of atoms and intervening space, with the former atoms matter is everywhere present, and there is no intervening space unoccupied by it. In gases the atoms touch each other just as truly as in solids. In this respect the atoms of water touch each other whether that substance be in the form of ice, water or steam; no mere intervening space is present. Doubtless the centres of force vary in their distance one from another, but that which is truly the matter of one atom touches the matter of its neighbours.

Hence matter will be *continuous* throughout, and in considering a mass of it we have not to suppose a distinction between its atoms and any intervening space. The powers around the centres give these centres the properties of atoms of matter; and these powers again, when many centres by their conjoint forces are grouped into a mass, give to every part of that mass the properties of matter. In such a view all the contradiction resulting from the consideration of electric insulation and conduction disappears.

The atoms may be conceived of as highly *elastic*, instead of being supposed excessively hard and unalterable in form; the mere compression of a bladder of air between the hands can alter their size a little; and the experiments of Cagniard de la Tour carry on this change in size until the difference in bulk at one time and another may be made several hundred times. Such is also the case when a solid or a fluid body is converted into vapour.

With regard also to the *shape* of the atoms, and, according to the ordinary assumption, its definite and unalterable character, another view must now be taken of it. An atom by itself might be conceived of as spherical or spheroidal, or where many were touching in all directions, the form might be thought of, as a dodecahedron, for any one would be surrounded by and bear against twelve others, on different sides. But if an atom be conceived to be a centre of power, that which is ordinarily referred to under the term *shape* would now be referred to the disposition and relative intensity of the forces. The power arranged in and around a centre might be uniform in arrangement and intensity in every direction outwards from that centre, and then a section of equal intensity of force through the radii would be a sphere; or the law of decrease of force from the centre outwards might vary in different directions, and then the section of equal intensity might be an oblate or oblong spheroid, or have other forms; or the forces might be disposed so as to make the atom polar; or they might circulate around it equatorially or otherwise, after the manner of imagined magnetic atoms. In fact nothing

can be supposed of the disposition of forces in or about a solid nucleus of matter, which cannot be equally conceived with respect to a centre.

In the view of matter now sustained as the lesser assumption, matter and the atoms of matter would be mutually penetrable. As regards the mutual penetrability of matter, one would think that the facts respecting potassium and its compounds, already described, would be enough to prove that point to a mind which accepts a fact for a fact, and is not obstructed in its judgement by preconceived notions. With respect to the mutual penetrability of the atoms, it seems to me to present in many points of view a more beautiful, yet equally probable and philosophic idea of the constitution of bodies than the other hypotheses, especially in the case of chemical combination. If we suppose an atom of oxygen and an atom of potassium about to combine and produce potash, the hypothesis of solid unchangeable impenetrable atoms places these two particles side by side in a position easily, because mechanically, imagined, and not unfrequently represented; but if these two atoms be centres of power they will mutually penetrate to the very centres, thus forming one atom or molecule with powers, either uniformly around it or arranged as the resultant of the powers of the two constituent atoms; and the manner in which two or many centres of force may in this way combine, and afterwards, under the dominion of stronger forces, separate again, may in some degree be illustrated by the beautiful case of the conjunction of two sea waves of different velocities into one, their perfect union for a time, and final separation into the constituent waves, considered, I think, at the meeting of the British Association at Liverpool. It does not of course follow, from this view, that the centres shall always coincide; that will depend upon the relative disposition of the powers of each atom.

The view now stated of the constitution of matter would seem to involve necessarily the conclusion that matter fills all space, or, at least, all space to which gravitation extends (including the sun and its system); for gravitation is a property of matter dependent on a certain force, and it is this force which constitutes the matter. In that view matter is not merely mutually penetrable, but each atom extends, so to say, throughout the whole of the solar system, yet always retaining its own centre of force. This, at first sight, seems to fall in very harmoniously with Mossotti's mathematical investigations and reference of the phenomena of electricity, cohesion, gravitation, &c. to one force in matter; and also again with the old adage, "matter cannot act where it is not." But it

is no part of my intention to enter into such considerations as these, or what the bearings of this hypothesis would be on the theory of light and the supposed æther. My desire has been rather to bring certain facts from electrical conduction and chemical combination to bear strongly upon our views regarding the nature of atoms and matter, and so to assist in distinguishing in natural philosophy our real knowledge, i.e. the knowledge of facts and laws, from that, which, though it has the form of knowledge, may, from its including so much that is mere assumption, be the very reverse.

I am, my dear Sir,

Yours, &c.,

MICHAEL FARADAY.

DIVISION VII.

ON THE ANALOGIES BETWEEN THE UNDE-COMPOUNDED SUBSTANCES; SPECULATIONS RESPECTING THEIR NATURE; ON THE MODES OF SEPARATING THEM, AND ON THE RELATIONS OF THEIR COMPOUNDS.

1. *Of the Analogies between the undecomposed Substances ; Ideas respecting their nature.*

1. The undecomposed substances most analogous to each other, are certainly to be found amongst the metals; some of these are so similar that it requires refined observation, and sometimes experiment to distinguish them. There is likewise a chain of gradations of resemblance which may be traced throughout the whole series of metallic bodies, at the same time that certain similar and characteristic properties are found to belong to metals in other respects most unlike each other.

Silver and palladium, antimony and tellurium, agree in a great number of qualities. Potassium and platinum, if we except their lustre, colour, and power of conducting electricity, are bodies extremely dissimilar; yet, by arranging

the metals in the order of their natural resemblances, these two substances may be made parts of one chain of natural bodies: potassium, sodium, and barium are very like each other; barium approaches to manganese, zinc, iron, tin, and antimony. Platinum is analogous to gold, silver, and palladium; and palladium is connected by distinct analogies with tin, zinc, iron, and manganese. Arsenic and chromium, though amongst the most dissimilar of the metals in other respects, agree in the property of forming acid matter by combination with oxygen.

Amongst the inflammable bodies not metallic there are analogies, but not a similar series. Sulphur and phosphorus agree in many respects; carbon and boron are likewise analogous, and are connected by distinct relations with the metallic substances. Azote, whilst it agrees with the other combustible bodies that have been named in forming an acid by saturation with oxygen, is analogous to carbon in its incapacity of uniting to chlorine.

Chlorine and oxygen are separated from the inflammable bodies by a number of marked distinctions; yet sulphur agrees with chlorine in forming an acid by combining with hydrogen; and has a weak attraction for chlorine and a strong attraction for metallic substances.

2. As far as our knowledge of the nature of compound bodies has extended, analogy of properties is connected with analogy of composition; if one of the inflammable solids or metals is proved to be compound, there would be strong evidence for supposing that the others were likewise compounded. It has been already mentioned that sulphur and phosphorus, when Voltaic electrical sparks are taken in them in a state of fusion, afford hydrogen gas. I found likewise that when an alloy of tellurium and potassium was acted upon by melted sulphur, telluretted and sulphuretted hydrogen equal to at least 80 times the volume of the sulphur were disengaged. I have made many experiments of this kind with similar results, the sulphur being recently sublimed in azote, and moisture being excluded with the greatest care. In the experiments of Voltaic electrization, it might be supposed that the hydrogen being only in very small quantity might belong to an accidental admixture in the sulphur and the phosphorus; but the proportion is too large in the experiments on the action of tellurium potassium and sulphur, to allow of a similar inference, and it seems more probable that it arises either from the decomposition of the sulphur, or of the metals, or all of these bodies.

3. We know nothing of the true elements

belonging to nature ; but as far as we can reason from the relations of the properties of matter ; hydrogene is the substance which approaches nearest to what the elements may be supposed to be. It has energetic powers of combination, its parts are highly repulsive as to each other, and attractive of the particles of other matter ; it enters into combination in a quantity very much smaller than any other substance, and in this respect it is approached by no known body.

After hydrogene oxygene partakes most of the elementary character ; it has perhaps a greater energy of attraction, and next to hydrogene is the body that enters into combination in the smallest proportion.

4. I have already hinted at the idea that all inflammable matters may be similarly constituted, and may contain hydrogene. And on this supposition they may be conceived to owe their powers of combining both with oxygene and chlorine, to the attractive energies of their combined hydrogene.

On the most probable view of the nature of the amalgam from ammonia, as I have mentioned, it must be supposed to be composed of hydrogene, azote, and quicksilver ; and it may be regarded as a kind of type of the composition of the metals ; and by supposing them and the inflammable bodies different combina-

tions of hydrogene with another principle as yet unknown in the separate form ; all the phenomena may be easily accounted for, and will be found in harmony with the theory of definite proportions.

The metal of ammonia or *ammonium* must be supposed to be constituted by 8 of hydrogene, and 26 of azote ; and as azote unites to five proportions five times 15 of oxygene, it may be supposed to contain ten proportions of hydrogene ; and its constitution may be thus expressed, 10 proportions of hydrogene and 16 proportions of an unknown basis. Ammonium, on the same hypothesis, will consist of 16 unknown basis, and 18 hydrogene. Potassium, the number representing which is 75 ; as it combines with 3 proportions of oxygene, may be supposed to consist of 69 unknown basis, and 6 hydrogene. Sodium, which is represented by 88, and which likewise combines with three proportions of oxygene, may be considered as consisting of 82 basis, and 6 hydrogene. Tin, the number of which is 110, and which combines with two proportions of oxygene may be supposed to be constituted by 106 of basis and 4 hydrogene ; and silver, which is represented by 205, of 203 of basis, and 2 hydrogene. Amongst the acidifiable bodies, sulphur, which is represented by 30, may be supposed to consist of

6 hydrogene, and 24 basis; Phosphorus of 4 hydrogene, and 16 basis; and charcoal of 4 hydrogene and 7.4 basis. It will be unnecessary to supply any more of these estimations, the principles of which are obvious; and in an elementary book it would be improper to dwell upon matters of mere speculation; even these transient views have been developed merely for the sake of pointing out a promising path of enquiry.

5. In supposing the quantity of hydrogene in the inflammable solids and metals denoted by the quantity of oxygene or of chlorine they absorb, it is taken for granted that the hydrogene forms only water or muriatic acid in the new combination, but it is possible that hydrogene may combine with oxygene and chlorine in many different proportions, and that its union with a peculiar basis may modify its power of attraction; so that even allowing the general hypothesis, no confidence can be placed in the numerical expressions of the proportions of hydrogene and basis; they are offered merely as possible circumstances.

6. The probabilities that the metals and inflammable solids may be constituted by different and various proportions of hydrogene and an unknown basis, are however strengthened by

the fact, that the metals in which hydrogen is supposed to be attracted by the largest quantity of other matter are the least disposed to combine with oxygen and chlorine; and those that are supposed to contain the largest quantity of hydrogen to the smallest quantity of other matter, are the most combustible, and likewise those supposed to contain the largest, and consequently the least attracted quantity of hydrogen, have the lowest specific gravity.

7. When the analogy of the oxides to many of the hydrates, and that of the combinations of chlorine to many of the neutral salts, is considered, bodies so much alike that till lately they have been confounded together; the view that the inflammable bodies contain hydrogen becomes still more likely. Water cannot be separated from the hydrates of potassa or soda by heat; and the hydrate of lime is extremely analogous to the pure earth; and supposing the oxides to be compounds of unknown bases and water, it might be expected that the water would adhere to them with great energy, and would only be separated in consequence of the bases entering into a new combination.

Common salt is very analogous to sulphate of potassa and other bodies known to consist of acid matter and alkaline matter; and if sodium

consist of a basis combined with hydrogen, then common salt may be considered as composed of the same basis united to muriatic acid.

8. Chlorine and oxygen agree in many of their characters ; but the weight of chlorine, its colour, its absorbability by water are all in favour of its being a compound. The number representing chlorine is so high that it may include four proportions of oxygen ; and if this body be supposed to consist of oxygen united to an unknown basis, the analogy of the combinations of chlorine, both to the oxides and the salts, might be easily explained. The evidences in favour of such an idea of the constitution of chlorine are, however, much inferior to those which render it probable that the inflammable solids contain hydrogen ; and this speculation on the composition of chlorine must not be confounded with the notion that chlorine is a compound of oxygen and muriatic acid free from water ; for supposing a basis to exist in chlorine, it does not follow that it will be acid in its nature. The characteristic acid belonging to the combinations of chlorine is formed by the union of that body with hydrogen ; and sulphur likewise forms an acid by combining with hydrogen.

9. I have mentioned, page 172, that in the electrization of a globule of mercury in water,

oxygen appears to be combined with the metal, and yet no hydrogen evolved. I have made a number of experiments on this subject, and have ascertained that, in the process described, oxide is formed, without any apparent compensation in the production of inflammable matter; nor was I able to detect any combination into which the hydrogen could have entered; so that these experiments, as they now stand, would induce the belief that water is the ponderable basis of both oxygen and hydrogen, and that these two forms of matter owe their peculiar properties either to the agency of imponderable substances, or to peculiar arrangements of the particles of the same matter; but such a formidable conclusion as this must not be hastily adopted, for in all other cases oxygen and hydrogen appear as perfectly inconvertible substances, and in no other instance can one be procured from water without the correspondent quantity of the other, or without some product in which the other may be supposed to enter. In all cases in which the circuit appears to be interrupted, even this is the case. When the finger is plunged in a glass of water connected with a wire of platina positively electrified from the battery of 8000 double plates of the Royal Institution, oxygen is produced, and there is no appearance of hydrogen; but in this case

the body is connected with a floor containing moisture, and at the extreme point of the moist surface, where it is in contact with a metallic body, hydrogene must be disengaged; and the same changes occur if a circuit be made through eight persons, their hands being in contact, the two forming the extremity of the chain, having their fingers plunged in two glasses connected by wires of platinum with the two poles of the battery; hydrogene is produced from one wire, and oxygene from the other. Till I ascertained that even acids, and alkalis could be attracted from a central vessel in the Voltaic circuit to the two extremities of the positive and negative metallic surfaces, it appeared very mysterious that oxygene and hydrogene should be separately produced in the Voltaic electrization of water; but if it be possible for lime to be attracted through sulphuric acid to the negative surface, it seems equally possible that hydrogene may be attracted through the moisture in a living body; or a series of decompositions and recompositions may be simultaneously produced throughout the whole extent of the moist surface, by which, whilst a particle of oxygene is produced at one extremity of the chain, a particle of hydrogene is evolved at the other.

10. There is, however, no impossibility in the

supposition that the same ponderable matter in different electrical states, or in different arrangements, may constitute substances chemically different: there are parallel cases in the different states in which bodies are found, connected with their different relations to temperature. Thus steam, ice, and water, are the same ponderable matter; and certain quantities of ice and steam mixed together produce ice-cold water. Even if it should be ultimately found that oxygene and hydrogene are the same matter in different states of electricity, or that two or three elements in different proportions constitute all bodies, the great doctrines of chemistry, the theory of definite proportions, and the specific attractions of bodies must remain immutable; the causes of the difference of form of the bodies supposed to be elementary, if such a step were made, must be ascertained, and the only change in the science would be, that those substances now considered as primary elements must be considered as secondary; but the numbers representing them would be the same, and they would probably be all found to be produced by the additions of multiples of some simple numbers or fractional parts.

11. That the forms of natural bodies may depend upon different arrangements of the same particles of matter has been a favourite hypothesis

advanced in the earliest era of physical research, and often supported by the reasonings of the ablest philosophers. This sublime chemical speculation sanctioned by the authority of Hooke, Newton, and Boscovich, must not be confounded with the ideas advanced by the alchemists concerning the convertibility of the elements into each other. The possible transmutation of metals has generally been reasoned upon, not as a philosophical research, but as an empirical process. Those who have asserted the actual production of the precious metals from other elements, or their decomposition, or who have defended the chimera of the philosopher's stone, have been either impostors, or men deluded by impostors. In this age of rational enquiry it will be useless to decry the practices of the adepts, or to caution the public against confounding the hypothetical views respecting the elements founded upon distinct analogies, with the dreams of alchemical visionaries, most of whom, as an author of the last century justly observed, professed an art without principles, the beginning of which was deceit, the progress delusion, and the end poverty.

THE CHEMICAL NEWS.

VOLUME XX.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 501.—FRIDAY, JULY 2, 1869.

THE FARADAY LECTURE,

DELIVERED BY

M. J. DUMAS,

Senateur; Président de la Commission des Monnaies et Médailles; Member, and one of the Perpetual Secretaries, of the Institut; Inspecteur Général de l'Enseignement Supérieur; President de la Société d'Encouragement pour l'Industrie Nationale; Grand Croix de la Légion d'Honneur, &c., &c.

BEFORE THE

CHEMICAL SOCIETY OF LONDON,

IN THE

THEATRE OF THE ROYAL INSTITUTION,

THURSDAY, JUNE 17TH, 1869.

GENTLEMEN,—You have desired that the memory of Faraday should be handed down to posterity; you have summoned together men of science, all to celebrate, in a solemn manner, his great and beneficial labours; and, calling upon France to take the lead in this solemnity, you have chosen me to be his panegyrist, no doubt on account of the long and constant friendship with which I was honoured by Faraday.

I am the bearer of the acknowledgments of the scientific men of France, as well as my own. My country—I am proud to say it—can offer representatives of science much more worthy of your approbation; but I know no one, at least, who feels more intimately the sentiments of profound gratitude for the noble welcome which England has accorded for so long a time, nor do I know one who bears so sincere a veneration for Faraday.

The name of your illustrious fellow countryman is not one which any single nation can claim as its exclusive property; his labours and discoveries are as widely recognised in France, in Germany, and in America as in England. Faraday belongs to the whole world. There is not a spot on this earth to which civilisation has penetrated, that does not claim the right of partaking of the respect and gratitude you entertain for him.

Faraday was identified with the scientific movement of the first half of this century; he was one of its principal leaders, and drew in his train a whole host of thinkers, engineers, men of enterprise, and capitalists. Ever contemplating the chaste beauties of nature, and searching into her most hidden recesses, this disinterested philosopher, this deep thinker, scattered broadcast on his path the seeds of

the most extraordinary and unheard-of results—such are the electric currents of Faraday that bear our messages, furrowing Europe and traversing the Atlantic—such are those lights, rivalling the sun in brilliancy, which shine forth from our principal lighthouses; and it is even to the gases which he liquefied that hot countries owe the luxury of ice.

In the pursuit of truth alone, he was able to satisfy, as if by accident, the boldest demand of a refined civilisation; and, devoted to the ideal, he sowed the seed of riches, not for himself, for he despised them, but for the profit of trade, which has gathered the fruit.

Faraday is the type of the most fortunate and most accomplished of the learned men of our age. His hand, in the execution of his conceptions, kept pace with his mind in designing them; he never wanted boldness when he undertook an experiment, never lacked resources to ensure success, and was full of discretion in interpreting results. His hardihood, which never halted when once he had undertaken a task, and his wariness, which felt its way carefully in adopting a received conclusion, will ever serve as models for the experimentalist.

The study of nature entirely puts aside conjecture, and places a guard on vague hypotheses; it begins with facts, ascends to laws, and raises itself, as far as the limits of man's intellect will permit, to the knowledge of causes, by the triple means of observation, experiment, and logical deduction. A long familiarity with the exact detail of phenomena can alone give to a man, as to Faraday, the right of being bold; he is, like Faraday, restrained when he has a thorough appreciation of the limits of man's knowledge. It is two centuries ago since Europe received this system of philosophy from Galileo and Newton, characterised at that epoch by the establishment of the Academy of Naturæ Curiosorum, in Germany, which represented the art of observation; in Italy, by the Academia del Cimento, the school of experimental science; and in England and France, by the Royal Society of London and by the Académie des Sciences de Paris, which adopted mathematical science as one of the means most conducive to the knowledge of truth in the domain which is accessible to us.

What an awakening for Europe! After two thousand years, she found herself in the same position to which she was raised by the profound intellect of India, and the acute genius of Greece, by Aristotle, Plato, Archimedes, and their emulators, from which, during those long ages, she was permitted to fall, whilst the work of the assimilation of races

was being carried on under the political influence of Rome.

What would have been the result if the learning of the Greeks, continuing its development from the third century before Christ to our own days, had pursued its triumphant march without hindrance? We do not know; no more than we can forecast the material resources of the human race after twenty centuries, nor to what heights the science of nature will have risen, should no social revolution create a breach in its tradition or retard its progress.

Greek art presents inimitable models; Greek philosophy has forestalled the modern schools in all their fearless opinions; and Greek science, not less prolific, paved the way which Europe has followed after long hesitation.

It is not difficult to connect Leucippus, a contemporary of Alexander the Great, who first clearly enunciated the philosophical doctrine of atoms, and the illustrious physicist of Manchester, Dalton, who, at the commencement of this century, founded, upon experiment, the atomic theory of modern chemists. Between these two points, so far removed, there is no intermediate link. Dalton is the son of Leucippus. Thus Cuvier, too, whose inventive genius was greater than that of Aristotle, was the sole inheritor of his spirit of order, his love of method, and his strength of judgment. In the same manner, we may ascend directly from Galileo and Newton, to Archimedes and Plato; the ideas of Faraday, too, on matter, atoms, force, and motion, were those of a Greek philosopher. The Romans did not receive this inheritance from the Greeks; given more to practical pursuits, they did not recognise the fact that these owed their progress to pure theory.

Truth is so beautiful that it deserves every effort a man can bestow to gain it; it is so fruitful that it carries along with it its own recompense. In placing before our mind the end, without occupying ourselves with particulars, we find the ordinary details of well-being and riches fall into their proper places.

Has not the atomic theory of Dalton, in assigning limits to phenomena, renewed the whole art of chemistry? Has Lavoisier's theory of combustion ever ceased to direct agriculture, the useful arts, health, and therapeutics? Did not these two philosophers contemplate abstract truth in all its splendour, and after receiving it from above, was it not sufficient for them to cast their eyes upon the earth, to reflect its light, and to spread far and wide its fruitful and exhaustless seed?

Let us, then, continue faithful in the cultivation of science for itself, and trust, without anxiety, that it will bear practical fruit for itself. Our remembrance of the life of Faraday teaches us that moral truth, when implanted in a man's heart, develops, at the proper time, each virtue that life exacts. His labours show us that the same holds good with scientific truth. At the proper time, it produces, as well as many spontaneous fruits, each of those discoveries which civilisation demands.

To a nation ambitious of becoming famous in history, it should be said "Despise conquest, abandon the pursuit of riches, and seek Truth, for by that your memory will be perpetuated." In like manner it may be said to a people who desire war or fear it, who wish to remain agriculturists or seek the advantages of commerce; "Search for Truth; it will create your means of defence or attack, maintain the fertility of your plains, and furnish your manufactories with

resources against competition." The princes of by-gone times considered themselves enriched and assured of prolonged youth, if they could obtain an alchemist capable of making gold, and possessed of a panacea against mortality. The nations of the present day, better advised, seek the aid of chemistry, and place in its counsels their hopes of well-being and honest gain: they know the value of artificial soda, chlorine, gas illumination, stearine candles and aniline dyes, and are grateful for the labour and care which these discoveries have cost.

Everything must give way to the laws of nature, and he only who has mastered those laws can control her processes. But the mastery cannot be obtained without a struggle; the fable of Proteus is a true picture of the combat between man, eager for knowledge, and the stubborn guardian, charged with the preservation of the secrets of destiny. Proteus changed himself into a thousand shapes before speaking, and yielded only to the hero who, far from being moved by his transformations, bound him with bands of increasing pressure. Such is nature herself, her answers are always true, but like the ancient shepherd of Neptune's flocks, before allowing Truth to shine forth, she arrays herself in the garments of error, or hides herself behind the phantoms of illusion; and will only assume her proper shape under the determined pressure of a resolute disciple of Science. This indomitable courage was possessed by Faraday in the highest degree.

The struggle for mastery is often prolonged. The whole life of a man does not suffice; the meeting of many philosophers animated by the same idea, or even the labours of different generations devoted to one pursuit, are required for the attainment of success; hence free associations for the cultivation of physical science and laboratories, where young men full of faith and ardour, working under one head, unite in the execution of such plans as he may invent or approve. Private study, which was perhaps best adapted to Faraday's temperament but which prevented him from establishing a school, has been succeeded by the labours in common of learned societies, and work carried on simultaneously by pupils in the same laboratory. Enlightened countries at last comprehend that all scientific research is a battle to be won, and that every victory increases national power. Intelligent nations no longer deny to scientific men, worthy the name of captain, either arms for the contest, soldiers devoted to their cause, or subsidies for their maintenance. Science is no longer an unrecognised power of which, nevertheless, much is expected; to day, every government which does nothing for it must expect to be vanquished by rivals, and to receive the censure of posterity for its want of forethought.

When Christopher Columbus set out for the conquest of the New World, did he not require ships, sailors, provisions, and ammunition? How then can the new world of science be conquered without assistance?

For textile manufactures there must be raw material, machinery, workpeople. The best workman in England, left to his own resources, would be unable to make an inch of cloth. It is the same with scientific discoveries; to weave the web, there must be raw material, laboratories, apparatus, and reagents. The more eminent a scientific man may be, so much the more is he powerless to resolve unaided all the questions which arise in his mind,

and to develop all the views suggested to him by the new aspects of nature, which his penetration has reached.

How many *chefs-d'œuvre* might have been lost to us if Raphaël, protected by an illustrious Pope, had not been the centre of a brilliant and devoted school, capable of sparing him the actual labour required to develop his ideas! What discoveries will be made when scientific masters of all countries, raised to their true position, are no longer limited in their resources, confined as to their means of execution, and obliged to do everything with their own hands!

The high position held by Faraday allows of such a comparison, and we may regret the loss of the discoveries which might have been added to those with which he has benefitted the world, if, like Raphaël, he would, or could, have founded a school. Learned societies formerly chose as a subject for their solemnities, an encomium on those monarchs or ministers whose protection they enjoyed. This meeting presents a spectacle more in conformity with the dignity of science: Faraday indeed raised himself above his fellows like a prince, but as a prince of thought; he exercised his power like a minister, but as a prime minister of the power and forces of nature.

His life is likewise an epoch of intellectual progress; and our immediate posterity will speak of such and such discoveries as having been made in the time of Faraday; sure of being as well understood as if referring to events in history, as being of the time of Elizabeth or Charlemagne.

But the life of Faraday is known to you, and you are familiar with his labours. I cannot fail of rendering that homage to his memory which he would have desired himself if, together with you, I review the progress of those sciences to which he was devoted.

Since the commencement of this century, three nations, animated with a noble spirit of rivalry—England, Germany, and France—have been contending for the first place in the study of physical science. Warranted, by turns, in claiming superiority, no one of them has dreamed, for one instant, of abdicating its claims. From this generous strife have sprung innumerable labours, the boast of our age, which will imprint a character upon it in history.

I do not wish to review, nor even to point out, the advantages that these nations have received from the liberal hand of science, but to bring before our minds the acquisitions to our knowledge of matter and force, to point out those fundamental ideas which have been brought to light, and to call to mind the part we must attribute to Faraday in this wonderful movement. I propose, then, to examine what we have learnt with regard to—1st, the nature of concrete matter; 2nd, the forces which it obeys; 3rd, the nature of truly-organised matter; 4th, the force which animates it.

The Greeks considered all matter divisible into four irresolvable elements, viz., earth, water, air, and fire, which are concrete representations of the abstract ideas solidity, liquidity, gaseous state, heat. So far they were guided by their senses; but they were of opinion that, finally, matter was made up of inaccessible atoms, and that variety, in the number or the arrangement of the latter, accounted for all the varieties in natural substances.

At the present day, with Lavoisier, we give the name of elements to all substances which we cannot

break up or resolve; but hold, with Dalton, that these elements are themselves made up of atoms which unite in different proportions, and with varying arrangements, to form different compounds.

To sum up, matter can be reduced to substances which no longer admit of reduction, and these substances are the elements of modern chemists; matter has only three forms, the solid, the liquid, and the gaseous, which stand for the elementary substances of the Greeks; matter is agitated by different motions, which may be all represented by one alone—heat—as all the rest may be transformed into it.

Lavoisier demonstrates that these are substances which cannot be resolved into simpler parts, and these he calls elements; Dalton asserts that the latter are substances combined in unvarying proportions, and he gives the name of atoms to these proportions reduced to their simplest form. Are not the elements of Lavoisier subject to decomposition in their turn? Cannot the methods recognised by Dalton be brought under a more general statement? May not chemistry be in the same state as astronomy with Kepler's laws, and is it not waiting for its Newton?

We are inclined to believe in the absolute simplicity of Lavoisier's elements when we consider,—1st, that, since the commencement of civilisation, no power at man's disposal, no natural action observed by him, has been able to break them up; 2ndly, that when converted into gas, their atoms occupy the same space as before; 3rdly, that in the solid state their atoms have the same volume when we deal with analogous elements; 4thly, that in the last case their forms are identical, so that they can replace and displace one another mutually in their compounds, without any great change of properties; 5thly, that the heat required by atoms for a change of temperature, is the same, no matter how they differ in weight; lastly, that in order to separate them when united, any atom whatever requires the same amount of electricity as any other. But, with the exception of inalterability, all these properties, not excepting the last, one of Faraday's best discoveries, are found in all compounds of the same order; we have, then, only a right to say that Lavoisier's elements are substances of the same order, and if we may say that they *cannot* be resolved, it is only because they *have not* been resolved.

We are inclined to think Lavoisier's elements further reducible from considering—1st, their number, which has risen in less than a century from thirty-one to sixty-five, and which grows rapidly; 2nd, their natural classification by families, the different numbers of which approach gradually, like terms in a continuous series; 3rd, their indubitable analogy with organic radicals, which are compounds.

In this way, Faraday's idea, that the atoms composing simple substances are collections of centres of force diversely arranged, may be defended. Chemical atoms would be the starting point of the analysis; mechanical atoms its last stage.

However, the question has entered upon another phase since the most recent discoveries. Natural philosophy has enabled us to determine the elements which are in incandescent matter, by means of the character of the spectrum formed by the latter.

The fact that Lavoisier's elements have resisted for the millions of years that they have been on the earth all the efforts of nature and of man to reduce them, is a characteristic of simplicity. Now we can

say that these elements have resisted every effort at destruction in space as well as in time. We find in the sun, in the fixed stars, in the nebulae, and in comets themselves—that is, within our system and without our system—the elements which we have known on earth; we find the same metals, hydrogen, nitrogen, &c.

When we are taught by the beautiful discoveries of Messrs. Janssen, Lockyer, and Frankland, that the protuberances on the sun are only incandescent hydrogen, we ask, How shall it be possible to reduce this element if the temperature of the sun do not suffice for its reduction?

As far as man can go back in time, as far as man can reach by observation in space, the concrete elements of matter present the same character as Lavoisier's elements.

In their abstract forms, reduced to mere centres of force, these elements, if such be the name for matter in its final state, belong to an immense tract, and soar up into a region of thought, inaccessible to man both in space and in time.

The examination into the modifications which have taken place in our ideas on the subject of force authorises us in going back to an age long before the commencement of this, for from thence the changes in our ideas take their date. Then matter used to be placed under the dominion of universal attraction, of motion, of light, of heat, of electricity, of magnetism, of chemical affinity, of cohesion, of the force of solution, of capillary attraction, and, later, of endosmose, &c.

It was no longer the philosophy but the mythology of Greece that served as a model. Natural forces occupied the position with regard to modern science that the divinities of old did with respect to Olympus, and people came to attribute to the former, as they had done to the latter, distinct and inalienable personalities.

At the present day, we know that light and heat have many properties in common, that electricity can be changed into magnetism, and *vice versa*, and that mechanical action can produce heat, magnetism, electricity, light. This correlation of physical force, as Mr. Grove calls it, the data for which were given by Ampère, Melloni, and before them by Sady Carnot, and confirmed by the crucial experiments of Faraday, remove all doubt. These forces are different modes of motion, and all these modes of motion can be transformed one into the other.

The man with vulgar cravings sought for the transmutation of matter, and failed to find it; he had little care for the transmutation of forces, the deep meaning of which none but the philosopher understood, and as a reward for the disinterestedness of the latter, the truth was revealed to him.

One of my most eminent fellow-labourers, one of my countrymen who has many friends here, and whom you have heard in this theatre, M. Henry Ste. Claire Deville, has just proved the existence of a close alliance between affinity and mere physical attraction, by the discovery of dissociation, which will influence the progress of chemistry materially.

We cannot deny that there exists close relationship between affinity on the one hand, and mechanical force on the other, when we see the decomposition of a body, such as marble when submitted to the action of a steady heat, come to a stand in the same way and from the same causes as the vaporisation of a liquid *in vacuo*.

This is the first step that has been taken to bring chemical phenomena under the laws of mechanics, and to justify Newton's view that chemical attraction was a particular case of universal attraction.

Has not Mr. Graham, in turn, reduced to causes purely mechanical the manifold effects of diffusion, of endosmose, of capillarity? Has not this illustrious philosopher been led by his latest researches to manifest, not only the metallic character of hydrogen by a memorable discovery, but to seize the very moment at which the phenomenon of the mechanical condensation of a gas by a porous body changes into a truly chemical combination?

There remains, then, universal attraction which, acting on heavy bodies, guides the motion of the stars as well as that of atoms; a motion which produces heat, light, electricity, and magnetism.

The study of matter leads us to the knowledge of an ever-increasing number of elements, and of simpler and simpler forces. Matter which was always believed to be conceivable and susceptible of transmutation, has resisted the efforts of man; whereas physical forces which were considered to be beyond his reach are shown to be ephemeral, and change one into the other readily.

But what relation connects gravitation with the other forces in nature? We know not; and Faraday, who has meditated on this point all his life, and who has thrown such vivid light on all its surroundings, has not made one step towards the solution of the problem.

What is the cause of gravity itself? We now know no more than was known two hundred years ago, in Newton's time.

What is meant by organic matter? If one were influenced by the views of the old chemistry, there would be no difficulty in replying. All organic matter originated in plants or animals; it was destructible by heat; it contained, generally, carbon and hydrogen, often oxygen, sometimes azote. Thus it was a compound of which carbon formed the fundamental element, destruction by fire the chief characteristic, but which, above all, derived its organic character from the circumstances of its origin.

At that time, no one thought of confounding organic chemistry and mineral chemistry. At the present day, this fusion exists in all purely chemical substances; only the terms of this assimilation are not understood. We are dazzled by a quibble. My age, and the share I have had in this movement in science, compel me to explain clearly my opinion, and to endeavour to put an end to the misconception.

The first studies we pursue on the chemical phenomena of life teach us that plants create, and animals destroy, organic matter. The sun appears as the agent by whose means this matter is produced, and combustion by the air that animals breathe, as the process that destroys them, in order to restore their elements to the state of "brut" matter.

The chemical forces placed at the disposal of life, descending on the earth under the forces of light, disappear by radiating off into space under the form of heat. An equilibrium obtains between the vegetable and animal kingdoms for receipts and disbursements, represented by these two forms of motion—light and heat; and the amount of animal life which may be developed on the globe is measured by the amount of food that vegetable life has prepared for it. The dark rays of heat appear to carry off from the earth that which radiant and brilliant light has spread over it.

On looking more closely into it, however, it was found that matter of organic origin was divided into two groups; one so rich in species that it surpasses all that has ever been imagined of the very numerous species of plants or animals described by naturalists; the other containing but a very few distinct species.

The first group constitutes the true organic species of chemists; that is to say, those which they have analysed, of which they have recognised the constitution, which they make by means borrowed from their own sciences, and of which they can, consequently, define the nature by analyses and syntheses.

Let us first attend to these matters. At what moment can they be characterised as organic?

Their origin does not suffice. In fact, carbon, hydrogen, oxygen, azote, can be withdrawn from plants or animals, and no one would find anything but mineral elements.

Oxide of carbon, carburetted hydrogen, cyanogen, water, and ammonia may meet in the produce of the constituents of plants or animals without anyone thinking of making organic substances from these binary compounds. But old chemists gave this name to alcohol, to vinegar, to the essence of bitter almonds, to urea, for example. Now, if there is any certain principle in science, it is this. Alcohol, vinegar, essence of bitter almonds, urea, although proceeding from plants or animals, have never lived, and will never live. They are subordinate products of life; they are not necessary instruments of life.

With regard to them, chemistry need no longer hesitate. This matter is formed in the manner of mineral matter. It shows all the conditions of its composition, its structure, and its properties. One circumstance only distinguishes it, and that, even, is not absolute. Generally, mineral matter is formed of simple elements, directly united. However, we perceive sometimes that certain composite groups may act like elements, may replace them or be replaced by them in combinations, without the latter changing their general character.

That which is the exception in mineral chemistry becomes the rule in organic chemistry. Lavoisier had the presentiment of this when he wrote—"Organic chemistry is the chemistry of compound radicals."

At this day, there is no longer any doubt. Cyanogen, cacodyle, the metallic radicals of Dr. Frankland, are well-known substances, offering all the chemical qualities of simple bodies, and nevertheless compound.

The substitutions admit of displacing and replacing one element by another, or even, at pleasure, by a compound radical in all the organic matter of chemists without changing its type. The converse is true: there is no impediment to replacing a compound radical by an element in a combination; and this change does not alter the type of it more.

Thus, the organic materials of which we speak are similar in all their conditions or qualities to mineral materials; 1st, they contain certain compounds which play the part of elements; 2nd, they assimilate with the oxides, sulphides, chlorides; with acids, bases and mineral salts in all their properties; 3rd, their radicals can replace the mineral elements, and be replaced by them; 4th, they can replace each other reciprocally.

Like "brut" bodies, these materials are susceptible of crystallisation, of volatilisation, without becoming decomposed; they form definite combinations, are incapable of life, and never have lived.

They thus resemble mineral matter in every respect, and where they differ from it is only that they have the general principles of compound radicals, whilst the mineral species have generally the principles of elements.

Analogies are even apparent in some numerical relations known to the elements of mineral chemistry, and to the radicals of organic chemistry. These relations are manifest in the two cases, for all elements susceptible of being arranged in series or natural families.

Thus, lithium, sodium, potassium, whose respective atomic weights are 7, 23, and 39, form a series of which the difference is 16. Magnesium, calcium, iron, whose respective atomic weights are 12, 20, 28, form a series whose difference is 8.

Thus all organic radicals offer the same condition. Methylium, ethylium, propylium, butylium, &c., give a series whose difference is 14, their respective atomic weights being 15, 29, 43, 57.

It seems natural to conclude from all this evidence, not that substances thus endowed and composed are organic because they are derived from organised beings, but rather that the elements of mineral chemistry may be complex.

In any case, the assimilation of the two chemistries becomes more and more near.

This picture would be incomplete if we did not add a few more features.

The radicals of mineral chemistry formerly numbered 30, and the combinations known in nature raised the number to some hundreds; at this day we count 65 elements, and some thousands of compounds or natural mineral species.

The chemist of the last century might study them one by one, and become acquainted with them all. Such is not the mission of the chemist of the present day; the species being realised, he tries to study them in groups; the potential species he tries to create. In nature, every element produces, on an average, eight or ten species. In the laboratory, every element may form thousands of the same order as the known mineral species.

The contrast is still more striking in organic nature. The animals and plants which cover the surface of the earth are counted by hundreds of thousands, and yet their tissues and their juices, submitted to chemical analysis, resolve themselves into no more than a few hundreds of distinct chemical species.

But the power of combination is such, among the special elements which form them, that it is by thousands that they have arisen; and if we calculate the number of combinations of this kind which may be realised, it seems as easy to count the grains of sand on one of the great shores of the sea as to say to what number of figures may be raised the organic species which the chemist has to produce.

Thus mineral or organic species, counted formerly by hundreds, are now counted by thousands for the first and by millions for the second.

Whence comes this fecundity for the formation of the so-called organic substances? Many circumstances contribute to it; but the first results from the almost incalculable number of the compound radicals which it can realise. Each of them being able to give birth to a prodigious number of combinations, organic chemistry counts a very great number of heads of tribes, and each tribe an infinite number of species. The latter, already multiplied in fact for simple radi-

cals, are much more so by the consequences of the fertile discovery of Mr. Williamson, which has taught us to unite two different radicals to each other, to bring them into a single system, and to produce with the latter as numerous compounds as were obtained from each of the isolated radicals. In consequence of the first and fundamental discovery of Mr. Graham, on the triple functions of phosphoric acid, which has been extended to the domain of organic chemistry,—for acids by M. Liebig,—for bases by M. Berthelot,—for alcohols by M. Wurtz, the result of this harmony of work, of which the immensity alarms the imagination, is that the atomic compounds with which we were chiefly engaged forty years ago, have not only been multiplied, but that they have been repeated by counterproofs. One might say, without forcing a metaphor, that we had visited and described all the rooms of the ground floor of the building; that Messrs. Graham and Liebig have revealed to us the existence of a first and second story, which repeated all their arrangements, and that Messrs. Berthelot and Wurtz have shown us that it was the same case in the basement and in the cellars. Thus five times more chambers or species have been produced at pleasure.

But, from all the sources of multiplication of substances with which organic chemistry is concerned, the most fertile is that of substitution; in fact, the discovery of the compound ammonias by M. Wurtz, and the labours of M. Hofmann which resulted from them, have produced a multitude of combinations, in which the atoms of hydrogen contained in ammonia are replaced by compound atoms performing the function of elements—that is to say, by organic radicals. If we apply the calculation to this special case, we even see that, with the known radicals employed to replace entirely, or in part, the hydrogen, or to replace each other mutually, we should henceforth be able to produce compounds derived from ammonia by hundreds of thousands or by millions.

How if we were to apply the same calculation, and the same prevision to all the types?

There is yet more. The chemist is not now, as formerly, obliged to derive all the substances that he produces by these means from those yielded by animals and vegetables; he creates them at will; he no longer needs, for his starting point, the action of solar light on plants. When he wishes to produce organic substances, he obtains his force by employing heat, formerly regarded as the true means of destroying them.

Not that he has succeeded in directly uniting carbon, hydrogen, oxygen, and nitrogen, so as to form organic substances; but, by the aid of heat alone, he first combines them two and two, and he thus forms carburetted hydrogen, carbonic oxide, cyanogen, water, and ammonia. Afterwards, by subjecting these first compounds to the action of suitable substances, and by the necessary artifices, he succeeds in regenerating, little by little, all the definite compounds of organic chemistry.

There is not a chemist who has not performed syntheses of this character; but the most striking is that of urea, by M. Wöhler; and the first, which have been grouped in a systematic manner are those which have been performed in Germany, by M. Kolbe; and especially those performed in France, by M. Berthelot, who has worked at them with great success, being the first to reproduce formic acid, and to combine directly carbon and hydrogen.

The function of the chemist changes, and becomes elevated. In presence of the numerous substances that his power evokes from the regions of the unknown, he owes his first attention to order, method, classification, and to nomenclature. But, once this first duty is fulfilled, he contemplates this innumerable host of forms, raised by his conceptions, or realised by his hands; and he applies to mathematics for a definition of the harmonies of numbers therein revealed; to mechanics, for a statement of the laws which their structures obey, or those which determine the stability of the material systems which they represent.

The Bible tells us that when God had formed, from dust, all the beasts of the earth, and all the fowls of the air, he made them pass before Adam, and that the name given to each by Adam is its true name.

In presence of this new creation, not of animated beings—whose appearance on earth depends on a power superior to his—but of harmonious forms which chemistry reproduces at will, always identical with each other, and always distinct from all others, man might sometimes forget that he has no longer merely to give names to the works of God, in order to remember that he has to name his own works.

If the discoveries which we have witnessed during the last half century do not justify pride, they at least excuse it. But, to bring back man to our appreciation of truth, it suffices to tell him that—if he has become more expert in the art of observing, if he employs with more certainty the art of experimenting, if the logic proper to the sciences leads him more surely to the discovery of the laws of nature—he has not as yet advanced one step towards the knowledge of causes.

Let us consider, in particular, what he knows on the subject of the materials which his life sets in motion in its development, and the contrast will be striking.

If I question the physiologist, on the subject of these millions, or milliards, of compounds, misnamed organic, of which the chemist transforms, reproduces, or creates at pleasure the species, he will reply to the three following questions:—Are these compounds living?—No! Have they lived?—No! Are they capable of living?—No!

If I ask the chemist himself if these compounds belong to mineral chemistry—to the chemistry of raw (brut) substances—he will reply, Yes!

Organised matter, not capable of being crystallised, but destructible by heat, the only matter which lives, or has ever lived—this matter, a subordinate agent of the vegetating power in plants, of the motion and sensation of animals, cannot be produced by chemistry; heat does not give birth to it; light continues to engender it under the influence of living bodies.

Let us not be disturbed by a quibble. The ancients admitted that nature alone produces organic matter, and that the art of the chemist is limited to transforming it. To-day we might, perhaps, even pretend that chemistry is powerful enough to replace, in all respects, the forces of life, and to imitate its processes; let us keep to the truth.

The ancients were mistaken when they confounded, under the name of *organic matter*, sugar and alcohol, which have never lived with the living tissue of plants or the flesh of animals. Sugar and alcohol have no more share of life than bone-earth, or salts contained in the various liquids. These remnants, or rubbish of life, placed amidst organic matter, are

true mineral species, which must be brought back to, and retained amongst, "brut" bodies. Chemistry may produce them in the same sense that she manufactures sulphuric acid or soda, without, for all that, having penetrated into the sanctuary of life.

This subject remains what it was—inaccessible, closed. Life is still the continuation of life; its origin is hidden from us as well as its end. We have never witnessed the beginning of life: we have never seen how it terminates.

The existing chemistry is, therefore, all powerful in the circle of mineral nature, even when its processes are carried on in the heart of the tissues of plants or of animals, and at their expense; and she has advanced no further than the chemistry of the ancients, in the knowledge of life and in the exact study of living matter; like them, she is ignorant of their mode of generation.

Where, then, is true organised matter, or matter susceptible of organisation? What is its chemical constitution? What is its mode of production? What is its manner of growth?

Instead of myriads of species, one would feel disposed to recognise but eight or ten at most, if one may be allowed to consider elementary types of organisation as chemical species. Be this as it may, in the origin of beings which have life we see cells appear, and in the heart of their types we find cells for organic elements, and, still beyond these, germs of cells.

In these cells, or in the spaces between them, we observe inert products, aliments, excretion, substances stored up. It is the cell, it is the germs which proceed from life, which live, which engender life, and then die. The substances which are contained in, or which surround these organs, are subordinate accidents, products rejected by organisation, or destined to its use, but distinct from life.

Every organised being is born of a germ; every plant from a seed; every animal from an egg. The physiologist has never seen the birth of a cell, excepting by the intervention or as the produce of a mother cell.

The chemist has never manufactured anything which, near or distant, was susceptible even of the appearance of life. Everything he has made in his laboratory belongs to "brut" matter; as soon as he approaches life and organisation, he is disarmed.

Thus, for a century past, the empirical elements of matter have been recognised and separated; their combinations have been multiplied to infinity; physical forces have been brought back to a common origin—motion—and one has been at pleasure changed into the other; and yet—

Is the intimate nature of matter known to us? No! Do we know the nature of the force which regulates the movement of the heavenly bodies and that of atoms? No! Do we know the nature of the principle of life? No!

Of what use, then, is science? What is the difference between the philosopher and the ignorant man?

In such questions the ignorant would fain believe they know everything; the philosopher is aware that he knows nothing. The ignorant do not hesitate to deny everything; the philosopher has the right and the courage to believe everything. He can point with his finger to the abyss which separates him from these great mysteries,—universal attraction which controls "brut" matter, life which is the source of organisation and of thought. He is conscious that

knowledge of this kind is yet remote from him, that it advances far beyond him and above him.

No, life neither begins nor ends on the earth; and if we were not convinced that Faraday does not rest wholly under a cold stone, if we did not believe that his intelligence is present here among us and sympathises with us, and that his pure spirit contemplates us, we should not have assembled on this spot, you to honour his memory, I to pay him once more a sincere tribute of affection, of admiration, and respect!

Section IV

KINETIC THEORIES

John Herapath submitted his paper, suggesting that the particles in gases were all in rapid translational motion, to the Royal Society; but it was turned down, and he therefore sent it to *Annals of Philosophy* instead. The mathematical parts of the paper have been omitted here, and only the introductory discussion has been reprinted. Herapath suggested that gases were all composed of hard particles, probably of only one kind. His paper seems to have aroused little interest; as did the somewhat later one of J. J. Waterston, who introduced elastic particles instead of hard ones. It was not until James Prescott Joule, James Clerk Maxwell, and Rudolph Clausius took up the theory that the scientific world had to take it seriously. Davy, who was one of the referees responsible for rejecting it, must have been repelled by the hard atoms of Herapath's theory, which were very different from his own views; and Maxwell proved subsequently that hard particles could not account for the phenomena.

In a different tradition, Fabrizio Mossotti's theory of matter involved two kinds of particle, matter atoms and aether atoms; like atoms repelling, and unlike attracting, each other. The mathematical treatment has been omitted here. Richard Taylor's *Scientific Memoirs* was a journal which contained entirely articles translated from foreign periodicals; many important papers were thus first brought to the attention of British scientists. Mossotti's theory attracted the attention of Faraday and of the choleric Charles Babbage, one of those responsible for the improvement of the Cambridge mathematical school in the second decade of the century, and the inventor of the calculating engine, the ancestor of our electronic computers. A series of treatises on natural theology had been endowed under the will of the eighth Earl of Bridgewater, and Babbage, who had written in 1830 of the decline of science—meaning mathematical physics—in England, felt that his branch of science had been neglected. He therefore wrote an 'extra' treatise, which contains the discussion of Mossotti's theory reprinted here. Thomas Exley tried, in a series of papers read to the British Association, to apply this theory in more detail; but it seemed necessary to make it more and more complicated to account for more facts.

Thomas Graham is best known for his work on the diffusion of gases. In this

paper he argues for the unity of matter; but his theory is different from the ordinary kinetic theory in that the motion of the particles is said to be inalienable, as it could hardly be if they often collided with each other. The motion envisaged must be some kind of vibration; the atoms must be running on the spot and not rushing hither and thither.

In 1859, a few weeks before the *Origin of Species* was published, almost as momentous a step took place in physics when Maxwell introduced statistical methods in his treatment of the dynamical [or kinetic] theory of gases. He was undoubtedly one of the greatest mathematical physicists of the century, responsible for putting Faraday's theories into mathematical form as well as for this development of the theory of gases. But he had also an unusual capacity for writing for a general audience; and the two papers reproduced here are very clear, and non-mathematical. The first, from *Nature* (which had been started by Norman Lockyer in 1869), is an account of the kinetic theory of gases, and of the introduction of statistical methods into physics from the social sciences. The second is from the ninth edition of the *Encyclopaedia Britannica*, an edition in which really outstanding contributors were given plenty of rope. The result in this case was a first-rate review article on atomic theory, seen particularly from the point of view of a physicist.

FURTHER READING

- W. H. Brock, 'The Selection of the Authors of the Bridgewater Treatises', *Notes and Records of the Royal Society*, XXI (1966), 162-79
- S. G. Brush, 'The Kinetic Theory of Gases', *Annals of Science*, XIII (1957), 188-98; 273-82; and XIV (1958), 185-96; 243-55
- S. G. Brush, *Kinetic Theory*, Oxford, 1965-6, 2 vols
- C. C. Gillespie, 'Intellectual Factors in the Background of Analysis by Probabilities', in A. C. Crombie (ed.), *Scientific Change*, London, 1964, pp. 431-53
- P. and E. Morrison (ed.), *Charles Babbage and his Calculating Engines*, New York, 1961
- G. R. Talbot and A. J. Pacey, 'Some Early Kinetic Theories of Gases: Herapath and his Predecessors', *British Journal for the History of Science*, III (1966), 133-49

On the Physical Constitution of the Universe. (In a Letter to Davies Gilbert, Esq. MP. FRS. &c.)

DEAR SIR,

In the following memoir, which I have to request you will do me the honour of submitting to the consideration of the Royal Society, I have endeavoured to unravel the causes of some of the leading phænomena of the universe, such as those of heat, gravitation, &c. That a correct judgment may the more easily be formed of the nature of this memoir, I have prefixed a brief account of the train of thought I pursued in my investigations, which will tend to throw a considerable light over what follows. And because I conceive no theory established, however well it may accord with phænomena, unless it can be shown all others do not, I intended to take a review of some of the principal hypotheses that have been advanced and supported by different philosophers, and to show wherein I think them defective; but afterwards considering that this would extend the memoir to a much greater length than I wish, and that I might probably be obliged to press a little hard on the favourite opinions of some respectable philosophers, I have for the present laid this design aside. For similar reasons I have omitted all comment and comparisons, except what are necessary for the elucidation of the subject. I have likewise, in consequence of a conversation that I lately had with W. Clayfield, Esq. materially changed the plan of this memoir, so as to render the connexion and dependence between the principles and consequences more apparent. And in order to trespass as little as possible on the time of the Royal Society, I have only demonstrated some of the elementary propositions; reserving the proofs of others to a future period, when, if the little that I have done receive the countenance of the Royal Society, I might be induced to take a more elevated view of the subject, and to touch upon other things that are not mentioned.

The Royal Society will easily perceive that I am indebted for the hint of the cause of gravitation to Sir Isaac Newton, though, perhaps, it will be found, that I have carried the idea much further, and have extended it to the development of a much greater variety of phænomena than he could have anticipated. It would be preposterous for me in this place to name other distinguished philosophers to whose accurate experiments and luminous views I have, in the course of my inquiries, been under great obligations; but I cannot let slip this opportunity of acknowledging, that if it shall appear I have been any way successful in my solitary rambles through these exalted regions, it is probably in a great measure owing to your kind encouragement and directions, and to the flattering approbation you were pleased to bestow on my juvenile efforts so long ago as the beginning of 1809, when I had the pleasure of being introduced to you by my late respected

friend W. Perry, Esq. of Winterbourne. Without such stimuli, I might never have had sufficient confidence in myself to tread those intricate and almost trackless paths of science.

An Analytical Inquiry into the Cause of Gravitation, Heat, &c.

Several years ago, namely, in July 1811, while amusing myself with calculating some of the lunar equations from theory, I was induced to try to compute the annual equation to the moon's mean motion, somewhat after the manner in which Newton has calculated the magnitude of the variation. The result of this calculation, which considerably exceeded the quantity given in the tables of Halley, the only ones I then had, very much surprised me. At first I thought I had committed some error, or made some erroneous assumption; but on re-examining the calculus, and making every allowance which I thought might have any influence, I satisfied myself, that as far as my fundamental principles were correct, nothing was neglected which could affect the result to any thing like the magnitude of the difference. At another time it occurred to me, that the quantity of the equation, as given in the tables, might possibly be itself too small. I, therefore, set myself about correcting it from the observations at the end of Halley's tables; but so far from solving the difficulty by this means, I found the difference much greater; for, as far as I remember, the maximum of the equation I found to be, instead of $11' 49''$, only about $11' 17''$; that is, but a few seconds greater than the quantity given in the very correct tables of Burg. Baffled, therefore, in this attempt to reconcile observation and theory, I conceived that the quantity determined from observation must be the result of two opposite equations, one of which had escaped the cognizance of theory. And in this opinion I seemed to be more confirmed by another calculation of this equation, by means of an exponential theorem I had just before discovered, and by observing that the computation of the same equation by Machin, on the principle of an equant, came out also much greater than the quantity by observation. It is true I was for a little while staggered in my opinion by the statement of Newton, in the scholium to prop. 35, book 3, of the Principia, in which he says, that he had calculated the mean greatest quantity of this equation from the theory of gravitation at $11' 49''$. But as I observed that he simply named the result without even hinting at the method of calculation, though just beneath, in the same scholium, he minutely enough describes his calculus of one or two other equations of considerably less difficulty; and as I had observed that the quantity I had brought out would coincide with his, if diminished in the ratio of the moon's synodical to her siderial period, I thought it very probable that Newton had pursued the same course that I had; and that finding his numbers would agree with observation, if diminished in the said ratio of the synodical to the siderial period,

he diminished them, thinking there might be a reason for it which he did not perceive; but not being thoroughly convinced, he chose rather to omit than describe a calculation, with every part of which he was not perfectly satisfied. This at least appeared to me a very plausible way of accounting for Newton's silence; but whether it be a correct one, it is, perhaps, not worth the trouble of discussing, especially since the complete calculation of this equation, by the celebrated Laplace, in the *Mécanique Céleste*, shows, that whatever may have been Newton's method, it was, as well as my own, much too loose and inaccurate to be depended on. It is, however, remarkable, that all, or most, of the calculations of the ann. equa. hitherto made from theory, give the quantity of this equation greater than observation; and this is even the case with Laplace's.

Having now, as I thought, satisfactorily accounted for the difference between Newton's numbers and mine, I became more strongly persuaded in myself that the tabular magnitude of the nn. equa. was the difference of two equations; and, therefore, I frequently tried to unravel the cause and magnitude of the indeterminate one, but without success. At length, about the middle of the following September (1811), my attention being involuntarily turned to a consideration of Newton's opinion respecting the cause of gravitation, I fancied that I saw a true solution of the difficulty in question, as well as a complete development of the cause of gravitation. If, argued I with myself, gravitation depends upon the action of an elastic medium, such as Newton supposes, which grows rarer and rarer as you approach the dense bodies of the sun and planets, there ought to be some reason for this variation of density; and as Newton has not, as far as I could perceive, given any, I began to consider what it might * be. And after some little thinking, it occurred to me, that if this medium be of the same nature as our atmosphere and other gaseous bodies; that is, if it be capable of being expanded by heat, and contracted by cold, then, the sun being a very hot body, and the heat being so much the greater the nearer we are to him, the density of the medium ought, therefore, to decrease with a decreasing, and increase with an increasing distance, the same as Newton would have it. And because we find by experience that dense solid bodies receive heat more strongly than much rarer ones, particularly than gases, the dense bodies of the planets being heated by the solar rays as well as by the medium about them, ought, it appeared to me, to be hotter than this medium, and consequently ought to produce the same effects on the medium as the sun, though not in so great a degree. Therefore if, as Newton imagines, the

* The only accounts I had seen of Newton's ideas of this subject were in his *Optics*, and at the end of the *Principia*. I have, however, lately read a letter that he wrote to Mr. Boyle, printed in Bishop Horsley's edition of his works, wherein he gives his opinion of this fluid medium as being of the same nature as our air.

particles of the planets be impelled towards the sun by the inequality of pressure on their further and nearer sides, the denser parts of the medium pressing more forcibly than the rarer, the same reason will likewise hold good why bodies should be impelled towards the planets and other material parts of the system.

And by considering these things further, it seemed to me that if such be the cause of gravitation, the intensity of the impelling force should be subject to the influence of two circumstances; namely, the number of particles in the central body, and their temperature; so that it becomes greater when either of these becomes greater, and less when it becomes less. But since the earth in its passage round the sun is sometimes at a greater and sometimes at a less distance from it; and since the regions which are nearer the sun are hotter than those which are more remote, the temperature, and consequently the attraction of the earth, should increase as the earth approached the sun, and diminish as it receded from it, so as to be greatest about the perihelion, and least about the aphelion. And this being the case, the moon must move in a contracted orbit, and swifter round the perihelion earth, and in a dilated orbit, and slower round the aphelion earth; by which means an equation to the moon's mean motion must be generated contrary to the ann. equa. and diminish it, the same as I had supposed some unknown equation ought to do with the theoretical annual equation to reduce it to the tabular.

Thus it happened that the inadequate method of computation I had adopted, brought out a quantity which so well accorded with my first theoretical views of the cause of gravitation, that I could not help placing great confidence in the theory I had embraced. I, therefore, carried on my speculations with that ardour which a strong prejudice in favour of the truth of my principles, and the sanguine hopes of succeeding in so great a problem as that of developing the cause of gravitation, might naturally be supposed to inspire; but I soon found that before I could proceed any further, I must establish the cause of heat, and reduce its phænomena to mathematical laws. This I at first attempted to do by endeavouring to find out the relation which should exist between the masses of the particles of the ethereal medium and their repulsive force, in an equation connected with their distances from the sun. But being disappointed in this, and a great number of other attempts that I made, I became much dispirited, and was often on the point of forming a resolution never to consider the subject again. Indeed I frequently wished to persuade myself that the discovery was altogether beyond the reach of human ability; and with this view tried to thrust it entirely from my mind. Yet sometimes, when my thoughts were involuntarily turned this way, the idea that two

inanimate bodies could act on each other at a distance without some other means than that of a mere tendency, or inclination, in them to approach, would appear so strongly unphilosophical, and the apparent coincidence of several phenomena, with conclusions I had drawn from my notions of gravitation, so very seductive, that I could not avoid thinking the views I had taken were tolerably correct; and that there was only wanting the direction of some happy idea, which patient perseverance might possibly attain, to set the whole in a clear and irrefragable light. Thus between hope and despair, between unceasing attempts and mortifying failures, I continued until May 1814, at which time my ideas of heat underwent a complete revolution. Previous to this time I had conceived heat to be the effect of an elastic fluid; and on this supposition had repeatedly attempted to reduce its laws to mathematical calculation; but uniform disappointment at length induced me to give this hypothesis a careful investigation, by comparing it with general and particular phenomena. The result of this investigation convinced me that heat could not be the consequence of an elastic fluid. At the time I was making this comparison, I took every opportunity of examining how far the other hypothesis (which until now I had forgot was sanctioned by the names of Newton and Davy) agreed with phenomena, and was so well pleased with its simplicity, and the easy, natural manner in which the different phenomena seemed to flow from it, that I regretted having neglected it so long, and determined to consider it more attentively. A difficulty, however, soon appeared in the application of this theory of heat to gaseous bodies, which I had some trouble to conquer; for as I still adhered to the hypothesis of gases being composed of particles endued with the power of mutually repelling one another, I could by no means imagine how any intestine motion could augment or diminish this power. Here then I was involved in another dilemma; but after I had revolved the subject a few times in my mind, it struck me that if gases, instead of having their particles endued with repulsive forces, subject to so curious a limitation as Newton proposed, were made up of particles, or atoms, mutually impinging on one another, and the sides of the vessel containing them, such a constitution of aeriform bodies would not only be more simple than repulsive powers, but, as far as I could perceive, would be consistent with phenomena in other respects, and would admit of an easy application of the theory of heat by intestine motion. Such bodies I easily saw possessed several of the properties of gases; for instance, they would expand, and, if the particles be vastly small, contract almost indefinitely; their elastic force would increase by an increase of motion or temperature, and diminish by a diminution; they would conceive heat rapidly, and conduct it slowly; would generate heat by sudden com-

pression, and destroy it by sudden rarefaction; and any two, having ever so small a communication, would quickly and equally intermix.

Besides these, other properties equally consistent and gratifying, presented themselves; but as these were merely loose views of the subject, I soon resolved to examine it more rigorously, and to try if I could not bring it to the test of mathematical laws. In this, however, I met with a difficulty considerably superior to any I had yet encountered in the course of my analysis, and which, before I overcame it, gave me more real uneasiness than, perhaps, it can be imagined it should. But the truth is, my views of the subject expanded so much as I proceeded that even in this early stage I fancied I perceived, in the solution of the problem I was about, not only the discovery of the cause of gravitation, but also of the causes of all the other phænomena of nature; and my thoughts were, therefore, turned upon it with an intenseness and anxiety which I never before experienced, and which can scarcely be appreciated except by those who have been placed in a similar situation. To meet now, therefore, when I thought I had almost completed the discovery, with an obstacle which it baffled my utmost efforts to surmount, and which threatened destruction to the fabric I had so laboriously endeavoured to raise, was a shock I had hardly philosophy enough to withstand. However, as I had proceeded so far, and had been so much led away by the seducing coincidence of the consequences of my theory with phænomena, I determined to examine it thoroughly, and, if I should find it erroneous, to publish it together with the illustration of its errors, that if it could do no other good, it might serve for a beacon to prevent others from running against the rock on which my hopes and expectations had been wrecked.

The obstacle to which I allude is this: I saw directly I began to consider circumstances attentively, that if the constitution of things be such as I supposed, the ultimate atoms of all bodies, and, therefore, the particles of these gases, which I looked upon to be no more than these ultimate atoms, must be absolutely hard; they must admit of no breaking, splitting, shattering, or any impression whatever; and yet if the gases are to maintain their elastic property, and this property be the result of the particles mutually impinging on one another and the sides of the containing vessel, the particles, or atoms, must likewise be elastic; that is, they must be soft; for elasticity, according to the ideas we have of it, is nothing but active softness. Therefore, it appeared to me that the ultimate atoms ought to possess two properties in direct contrariety, hardness and softness, which is manifestly impossible.

Having arrived at this conclusion, which appeared to render the probability of success of all future inquiries in this track desperate, it might be supposed that my efforts would have ter-

minated. Nor, perhaps, is there any thing that could have induced me to perplex myself any more with this subject ; but the resolution I had formed to examine it thoroughly, and a fondness for the plausibility of my preconceived notions that I could not shake off, and which would oftentimes, even against my inclination, prompt me to try to explain away the absurdity I had brought out. The first thing that suggested itself for this purpose was, that elasticity might spring from a different source to what was commonly believed, and might be the property of hardness ; for I observed that the harder the bodies are, generally speaking, the more elastic they are. Thus glass is very hard, and likewise very elastic ; and the same is true of steel, and most of the other metals. Upon this hypothesis, therefore, I now tried to investigate the laws of gaseous bodies ; and as far as I then carried my speculations, the conclusions I drew exactly coincided with phænomena. But reflecting more deeply on the subject, I convinced myself that, however well these inferences and phænomena might agree, elasticity could not be a property of hardness ; and, therefore, that the hypothesis I had assumed could not be correct. At length, after a great deal of intense and fruitless thought, I remembered that when, some years before, reading the vulgar doctrine of the collision of hard bodies, I was very far from being satisfied with it ; but looking upon it then as an abstract and almost useless subject, I could not summon resolution enough to give it a critical investigation. Being now, however, drawn to the point by my analytical inquiries, the recollection of this dissatisfaction excited me to consider the circumstances connected with it attentively. The result of this consideration was a theory for the collision of hard bodies, so very different from the received theory, that it was not until I had examined it in a variety of shapes, had brought it to the test of experiment by my mathematical investigation of the laws of gaseous bodies, and had found that a theory something like it had been formerly given by Wren and Huygens, that I could satisfy myself I had not committed some oversight. But having considered and reconsidered it many different ways, without discovering any thing that could militate against it, I proceeded to carry on my theory as far as I judged it would be wanted, and then assumed the following postulata as the basis of my future inquiries.

Postulata.

1. Let it be granted that matter is composed of inert, massy, perfectly hard, indestructible atoms, incapable of receiving any change or impression in their original figure and nature.
2. Let it be granted that all solid and fluid bodies have their smaller parts composed of these atoms, which may be of different sizes and figures, and variously associated, according to the manner which the constitution and nature of the bodies require.

3. Let it be granted that gaseous or aeriform bodies consist of atoms, or particles, moving about, and among one another, with perfect freedom.

4. Let it be granted that what we call heat arises from an intestine motion of the atoms, or particles, and is proportional to their individual momentum.

5. Let it be granted that a gaseous body of very great tenuity in its parts fills all space, and extends to its utmost limits.

I have purposely put these hypotheses (if indeed we can call those things hypotheses which have been deduced from the analysis of phænomena) into the form of postulata, to avoid being obliged to establish them by direct demonstration. It is not my intention, for the reasons I have already given in the beginning of this memoir, to make any comparative remarks on their relative simplicity and probability. I shall only say a few words for the purpose of explaining the difference between my views on certain points and those which have been taken by others.

One of the sublimest ideas of the ancients was, that there is but one kind of matter, from the different sizes, figures, and arrangements of whose primitive particles, arises all that beautiful variety of colour, hardness and softness, solidity and fluidity, opacity and transparency, &c. which is observed in the productions of nature. Our first two postulata do not necessarily require that there should be but one kind of matter; there may be several kinds. But since it seems possible to account for all the phænomena on the supposition of one kind only, and since nature is always disposed to employ the simplest machinery, probability is strongly in favour of the ancient idea. In fact it does not seem to be impossible, from some of the phænomena of light and other circumstances, to show that nature has embraced the simplest means, and has likewise, if not in the size, at least in the figure of the atoms, confined herself within certain limits. But these things are too recondite to be pursued in this memoir; and experiments have not yet furnished us with sufficient data to be able to exhibit the exact line and rule with which nature has laid out her work.

Philosophers, since the time of Newton, have taught us that the elasticity of gases is owing to a mutual repulsion between their particles, by which they endeavour to fly from one another; but by our third postulatam we have divested matter of this repulsive property, and nevertheless, as it will be seen, the laws of gaseous bodies, investigated under this point of view, agree mathematically with phænomena.

The advocates for the theory of heat by intestine motion have usually considered the temperature as measured by the velocity of vibration; and I am not aware that any of them have defined it otherwise. This will do very well for different temperatures of the same body; but it seems to require the theory I have given in the fourth postulatam to enable us, under all circumstances, to compare the temperatures of different bodies.

In the fifth postulatum I have given the fluid of Newton for explaining the cause of gravitation. This illustrious philosopher has so clearly developed his ideas of the nature and action of this ethereal fluid, that I have had scarcely any thing to do but to confirm them with the application of the principles of our third and fourth postulata. It is true that the novelty of the views I have been obliged to take, and the unbeatenness of the track, have rendered even this a task of some difficulty; but the results I have obtained will, I presume, convince the Royal Society that my efforts have not been wholly unsuccessful; and that this idea of Newton, which has, from the uniform want of success to demonstrate it, often been placed to the account of this great man's foibles, was not adopted upon light grounds, or without mature consideration.

OF THE COLLISION OF PERFECTLY HARD BODIES.

Definitions of Hardness, Softness, and Elasticity.

Def. 1.—That body is perfectly hard whose figure cannot be altered by any weight, or percussion.

Corollary.—Hence a perfectly hard body must also be perfectly entire; for if it be composed of parts, there may be a force sufficient to separate them, and then the figure would be changed, which is against the definition. By a hard body, I mean one without parts, unchangeable, and indivisible, such as, perhaps, the primary particles of matter are.

Def. 2.—The figure of a soft body yields to pressure, or percussion, without recovering itself again.

Cor.—Hence a soft body cannot be entire, but must be composed of parts, which, being displaced, retain whatever situation is given them.

Def. 3.—A perfectly elastic body, like a soft one, suffers its figure to be changed by force, but recovers it again with an energy equal to the force by which it was changed.

Cor. 1.—Therefore an elastic body does likewise consist of particles, which, like the particles of a soft body, may be deranged; but as soon as the power is overcome by which they were disturbed, they exert as much force in recovering their situation, as was used in depriving them of it.

Cor. 2.—Because an elastic body recovers its figure with the same force by which it was changed, as much motion is generated in the recovery as was destroyed in the loss of the figure.

ARTICLE XXIII.

On the Forces which regulate the Internal Constitution of Bodies. By O. F. MOSSOTTI.

From a Memoir addressed to M. Plana, published separately, and communicated by M. FARADAY, Esq., D.C.L., F.R.S., &c.

PRELIMINARY REMARKS.

1. **T**HE study of the phænomena of nature has led philosophers to consider bodies as being composed of molecules held in a state of fixed equilibrium at a certain distance from each other. Such a state requires that they should be endued with a certain action. Some peculiarities of this action we are already able to assign, but its complete characteristics are not yet well defined.

As the resistance opposed by bodies to compression increases indefinitely with the reduction of their volume, though their molecules have not come into contact with each other, it shows that the force which they exercise is repulsive at the least distances. At a distance greater than these, but still imperceptible, it must vary with great rapidity, and become attractive, in order that a steady equilibrium of the molecules may be possible; and finally, when it has become perceptible, it must decrease in the inverse ratio of the square of the distance, in order to represent the universal attraction. The limits of the distance at which the negative action becomes positive vary according to the temperature and nature of the molecules, and determine whether the body which they form be solid, liquid, or aëriform.

There is a class of phænomena, rather singular at first sight, in which however it appears that nature designed, by separating the forces which she employs, to present herself in all her simplicity. Such are the phænomena which constitute what we denominate *statical electricity*. It is well known with what admirable facility Franklin explained these phænomena, by supposing that the molecules of bodies are surrounded by a quantity of fluid or æther, the atoms of which, while they repel each other, are attracted by the molecules. It is known also how Coulomb subsequently proved that the force with which the repulsion of atoms and the attraction of the molecules are produced, is, like universal attraction, regulated by the law of the inverse ratio of the square of the distance. Indeed, the latter philosopher has substituted for the hypothesis of Franklin, which is that generally followed in England, Germany, and Italy, another hypothesis, in which a second fluid is supposed to perform the part assigned to matter in that of Franklin; and this mode of explaining the

phænomena has been more generally adopted in France. It is even asserted that the latter hypothesis is the only one that should be received, inasmuch as it has been completely confirmed by the results of the beautiful analysis with which M. Poisson has begun to enrich the Memoirs of the Academy of Sciences. But they who put forward this assertion have not paid due attention to the fact that, although this illustrious geometer has, for the purpose of establishing his calculations, adopted the language of his school, the inferences drawn from them are not more applicable to the one hypothesis than to the other. He sets out in fact with the principle, that, "If several bodies, being electric conductors, are placed in presence of each other, and attain a permanent state, the result of the actions of the electric layers which cover them, on a point taken anywhere in the interior of a body must, in that state, be null; otherwise the combined electricity which exists in the point under consideration would be decomposed; but this is contrary to the supposed state of permanence." Now if for this principle the following be substituted: "If several bodies, being electric conductors, are placed in presence of each other, and thus attain a permanent state, the result of the actions of the layers of electric fluid which cover them, and of the exterior layers of matter which are not yet neutralized, on the electric fluid at a point taken anywhere in the interior of a body, must, in that state, be null; otherwise the electric fluid which exists in that point would be displaced, which is contrary to the supposed state of permanence;"—and if we interpret accordingly the literal denominations employed by M. Poisson in his equations,—all his results will be equally true on Franklin's hypothesis. In general, the action of the condensed electric fluid will stand for that of the vitreous fluid; and the action exhibited by the matter, in proportion as it is deprived of a quantity of its electric fluid, will stand for that of the resinous fluid. There is one circumstance, however, which makes a difference between the hypothesis of Dufay or Coulomb and that of Franklin: it is this, that, according to the one, the two fluids are moveable in the bodies, while according to the other the electric fluid is, but the matter is not, moveable. As the equilibrium, however, requires that we should only regard the relative position, the mobility of the electric fluid alone is sufficient for its establishment.

Æpinus, who has reduced Franklin's hypothesis to the form of a mathematical theory, was the first to remark, that if it be the requisite condition for the equilibrium of the electric fluids of two bodies, in their natural state, that "the attraction of the matter and the repulsive action of the fluid of the first body on the fluid of the second should be equal, and *vice versa*," there are but three forces in operation; two of which are attractive, and but one repulsive. In other words, each of the two bodies attracts the fluid of the other, while the mutual repul-

sion of the two fluids constitutes only a single force, equal to each of the two attractive forces. If then, with the equilibrium of the fluids, it is desired to find the equilibrium of the masses also, an equal repulsion must be allowed between the molecules; since the bodies would otherwise forcibly attract each other. But such an attraction is contrary to what we learn from experience. He felt at first a strong objection to the admission of such a repulsive force between the material molecules, as being opposed to the idea entertained of their mutual attraction, which was so clearly demonstrated on Newton's principles. But a little reflection satisfied him that this admission contained nothing that was opposed to facts, or, as he might rather have said, that was not confirmed by facts. Universal attraction itself may follow as a consequence from the principles which regulate the electric forces: for if we suppose that, the masses being equal, the repulsion of the molecules of matter is a little less than their attraction of the atoms of the æther, or than the mutual repulsion of the atoms themselves, this will be sufficient to leave an excess of attraction which, being directly as the product of the masses and inversely as the square of the distance, would exactly represent the universal attraction.

2. While reflecting on these principles, in a course of lectures on natural philosophy which I gave at the University of Buenos Ayres, I conceived the idea, that if the molecules of matter, surrounded by their atmospheres, attract each other when at a greater, and repel each other when at a less distance, there must be between those two distances an intermediate point at which a molecule would be neither attracted nor repelled, but would remain in steady equilibrium; and that it was very possible this might be the distance at which it would be placed in the composition of bodies. I thought the idea of sufficient importance to fix it in my memory, but did not at the time pursue its development further.

On my return to Europe I learned, through the reading of some memoirs, and in the course of conversation with men of science, that the attention of geometers was particularly directed to the molecular forces, as being those which may lead us more directly to the knowledge of the intrinsic properties of bodies. I was thus led to recall my ideas on the subject, and set about subjecting them to analysis. The results of my first investigations I here submit to the judgement of philosophers.

I have supposed that a number of material molecules are plunged into a boundless æther, and that these molecules and the atoms of the æther are subject to the actions of the forces required by the theory of *Æpinus*, and then endeavoured to ascertain the conditions of equilibrium of the æther and the molecules. Considering the æther as a continuous mass, and the molecules as isolated bodies, I found that, if

the latter be spherical, they are surrounded by an atmosphere the density of which decreases according to a function of the distance which contains an exponential factor. The differential equation which determines the density being linear, is satisfied by any sum of these functions answering to any number of molecules. Whence it follows that their atmospheres may overlay or penetrate each other without disturbing the equilibrium of the æther. Proceeding in the next place to the conditions of equilibrium of the molecules, I observed that, for a first approximation (which may be sufficient in almost all cases), the reciprocal action of two molecules and of their surrounding atmospheres is independent of the presence of the others, and possesses all the characteristics of molecular action. At first it is repulsive, and contains an exponential factor which is capable of making it decrease very rapidly : it vanishes soon after, and at this distance two molecules would be as much indisposed to approach more nearly as they would be to recede further from each other ; so that they would remain in a state of steady equilibrium. At a greater distance the molecules would attract each other, and their attraction would increase with their distance up to a certain point, at which it would attain a maximum : beyond this point it would diminish, and at a sensible distance would decrease directly as the product of their mass, and inversely as the square of their distance.

This action, possessing all the properties with which we can presume that molecular action is endued, is the more remarkable as it has been deduced from those forces only whose existence was already admitted by philosophers, and whose law is characterized by such extraordinary simplicity. When tested in the explanation of the varied phenomena which are proper to it, it must lead, in case of failure, to the exclusion of those forces from amongst physical principles ; or, in case of success, establish their reality ; and thus mark in a striking manner the admirable œconomy of nature.

To apply the formulæ which we have found, for the purpose of representing molecular action, to the phenomena of the interior constitution of bodies, requires methods of calculation which are not yet developed, and which must become still more complicated when the arrangement of the molecules, their form and their density, are taken into consideration. I have thought it advisable, however, in consideration of the use to which it might be applied by able geometers, not to postpone the publication of this mode of viewing molecular action. It is a subject which appears to me entitled to the greatest attention, because the discovery of the laws of molecular action must lead mathematicians to establish *molecular mechanism* on a single principle, just as the discovery of the law of universal attraction led them to erect on a single basis the most splendid monument of human intellect, *the mechanism of the heavens*.

APPENDIX.

NOTE A.

ON THE GREAT LAW WHICH REGULATES MATTER.

EVER since the period when Newton established the great law of gravity, philosophers have occasionally speculated on the existence of some more comprehensive law, of which gravity itself is the consequence. Although some have considered it vain to search for a more general law, the great philosopher himself left encouragement to future inquirers; and the time, perhaps, has even now arrived, when such a discovery may be near its maturity. It would occupy too much space to introduce many illustrations of this opinion; there is, however, one which deserves attention, because it is not merely a happy conjecture, but the hypothesis on which it rests has been carried by its author, through the aid of profound mathematical reasoning, to many of its remote consequences.

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M. Mosotti* has shown, that by supposing matter to consist of two sorts of particles, each of which repels similar particles, directly as the mass, and inversely as the squares, of their distances; whilst each attracts those of the other kind, also according to the same law,—then the resulting attractions explain all the phenomena of electricity, and there remains a residual force, acting at all sensible distances, according to the law of gravity.

Many of the discoveries of the present day point towards a more general law; and many of the philosophers of the present time anticipate its near approach. Under these circumstances, it may be interesting as well as useful briefly to state the principles which such a law *must* comprehend; and to indicate, however imperfectly, the path to be pursued in the research.

If matter be supposed to consist of two sorts of particles, or rather, perhaps, of two sorts of centres of force, of different orders of density; and if the particles of each order repel their own particles, according to a given law, but attract particles of the other kind, according to another law,—then, if we conceive only one particle of the denser kind to exist, and an infinite

* Professor of Physics at the University of the Ionian Islands.—The paper of M. Mosotti has been translated, and published by Mr. R. Taylor, in the third number of the *Scientific Memoirs*; a work which it is proposed shall contain translations of all the most important *original* papers printed in foreign countries.

number of the other kind, that single particle will become the centre of a system; surrounded by all the others, which will form around it an atmosphere denser near the central body.

If we conceive a stream of particles, similar to those forming the atmosphere, to impinge upon it, so as just to overcome its resistance, they will, whilst continually producing undulations throughout its whole extent, gradually increase its magnitude, until it attains such a size, that the repulsion of the particles at its outer surface is just balanced by the attraction of the central particle. If the stream continue after this point is reached, the whole outer layer will be pressed a little beyond the limit of attraction, and will fly off at right angles to the surface, which might then be said to radiate.

If the whole of the space in which such a central particle with its atmosphere is placed, is itself full of atmospheric particles, then their density will increase in approaching the central body; and if a stream of such particles were directed towards the centre, they might produce throughout the atmosphere vibrations, which would be transmitted from it in all directions.

If two such central particles, with their atmospheres, exist at a distance from each other, they will be drawn together by a force depending on the *difference* between

the mutual repulsion of their atmospheres and central bodies respectively for each other, and the attraction of each central particle for its neighbour's atmosphere : and in order to coincide with the existing law of nature, this must be directly as the mass, and inversely as the square, of the distance. The other conditions which such a law must satisfy, are—

1. That the juxtaposition of such atoms must, in some circumstances, form a solid body.

2. In other circumstances, a fluid.

3. That again, in still other circumstances, its particles shall repel each other, or the body become gaseous.

4. In the first state the body must possess cohesion, tenacity, malleability, elasticity ; the measure and extent of each of which must result generally from the original law, and in each particular case from the constants belonging to the substance itself.

5. In the second, it must possess capillarity, susceptibility of being compressed without becoming solid, as also elasticity.

But besides these, the *central* atoms must admit of a more intimate approach, so that their atmospheres may

unite and form one atmosphere. This might constitute chemical union. Binary compounds might then (supposing the distance between the two central particles to be very small, compared with the diameters of the atmospheres) have atmospheres not quite spherical, and attracting differently in different directions; thus possessing polarity. Combinations of three or more atoms, as the central body of one atmosphere, might give great varieties of attractive forces. Each different combination would give a different atmosphere; and the equation of its surface might, perhaps, become the mathematical expression of the substance it constituted. Thus, all the phenomena produced by bodies, acting chemically on each other, might be deduced from the comparison of the *characteristic* surfaces of the atmospheres of their atoms. Another result, also, might ensue. Two or more central atoms uniting, might either not be able to retain the same amount of atmosphere, or they might possibly be able to retain a larger quantity. If the particles of such atmospheres constituted heat, it would in the former case be given out, and in the latter absorbed by chemical union.

Hence the whole of chemistry, and with it crystallography, would become a branch of mathematical analysis, which, like astronomy, taking its constants from observation, would enable us to predict the character of any new compound, and possibly indicate the source from which its formation might be anticipated.

For the sake of simplicity, two species of particles only have been mentioned above; but it seems more probable, that matter consists of at least three kinds.

Suppose each kind to repel its own particles; and supposing the central atom, whilst it repels similar particles, to attract those of the two other kinds; and moreover, that these latter were either repulsive, or indifferent to each other. We might then conceive matter to be made up of particles, each having a central point, with an atmosphere surrounding it, and this atmosphere again inclosed within another and larger one.

Under such circumstances, the outer atmosphere might give rise to heat and light, to solidity and fluidity, and the gaseous condition; to capillarity, to elasticity, tenacity, and malleability. The more intimate union of the central atoms, by which two or more become enclosed in one common atmosphere of the second kind, might represent chemical combinations, and perhaps that atmosphere itself be electricity. Possibly, also, this intermediate atmosphere, acted on by the pressure of the external one, and by the attraction of the central atom, might take the liquid form. These binary or multiple-combinations of the original atoms, and their smaller atmospheres, would still be enclosed in an atmosphere of the outer kind, which might be nearly spherical. The joint action of the three might, at sensible distances, produce gravity.

The reader should, however, bear in mind, that these hints are but thrown out as objects of reflection and inquiry; and that nothing but a profound mathematical investigation can establish them, or even give to them that temporary value which arises from any hypothesis, representing a large collection of facts.

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XV. *Speculative Ideas respecting the Constitution of Matter.*

By T. GRAHAM, F.R.S.*

IT is conceivable that the various kinds of matter, now recognized as different elementary substances, may possess one and the same ultimate or atomic molecule existing in different conditions of movement. The essential unity of matter is an hypothesis in harmony with the equal action of gravity upon all bodies. We know the anxiety with which this point was investigated by Newton, and the care he took to ascertain that every kind of substance, "metals, stones, woods, grain, salts, animal substances, &c.," are similarly accelerated in falling, and are therefore equally heavy.

In the condition of gas, matter is deprived of numerous and varying properties with which it appears invested when in the form of a liquid or solid. The gas exhibits only a few grand and simple features. These again may all be dependent upon atomic and molecular mobility. Let us imagine one kind of substance only to exist, ponderable matter; and further, that matter is divisible into ultimate atoms, uniform in size and weight. We shall have one substance and a common atom. With the atom at rest the uniformity of matter would be perfect. But the atom possesses always more or less motion, due, it must be assumed, to a primordial impulse. This motion gives rise to volume. The more rapid the movement the greater the space occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity. Matter is thus made to differ only in being lighter or denser matter. The specific

* From the Proceedings of the Royal Society, 1863, p. 620. Communicated by the Author.

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motion of an atom being inalienable, light matter is no longer convertible into heavy matter. In short, matter of different density forms different substances—different inconvertible elements as they have been considered.

What has already been said is not meant to apply to the gaseous volumes which we have occasion to measure and practically deal with, but to a lower order of molecules or atoms. The combining atoms hitherto spoken of are not therefore the molecules the movement of which is sensibly affected by heat with gaseous expansion as the result. The gaseous molecule must itself be viewed as composed of a group or system of the preceding inferior atoms, following as a unit laws similar to those which regulate its constituent atoms. We have indeed carried one step backward, and applied to the lower order of atoms, ideas suggested by the gaseous molecule, as views derived from the solar system are extended to the subordinate system of a planet and its satellites. The advance of science may further require an indefinite repetition of such steps of molecular division. The gaseous molecule is then a reproduction of the inferior atom on a higher scale. The molecule or system is reached which is affected by heat, the diffusive molecule, the movement of which is the subject of observation and measurement. The diffusive molecules are also to be supposed uniform in weight, but to vary in velocity of movement, in correspondence with their constituent atoms. Accordingly the molecular volumes of different elementary substances have the same relation to each other as the subordinate atomic volumes of the same substances.

But further, these more and less mobile or light and heavy forms of matter have a singular relation connected with equality of volume. Equal volumes of two of them can coalesce together, unite their movement, and form a new atomic group, retaining the whole, the half, or some simple proportion of the original movement and consequent volume. This is chemical combination. It is directly an affair of volume, and only indirectly connected with weight. Combining weights are different because the densities, atomic and molecular, are different. The volume of combination is uniform, but the fluids measured vary in density. This fixed combining measure—the *metron* of simple substances—weighs 1 for hydrogen, 16 for oxygen, and so on with the other “elements.”

To the preceding statements respecting atomic and molecular mobility, it remains to be added that the hypothesis admits of another expression. As in the theory of light we have the alternative hypotheses of emission and undulation, so in molecular mobility the motion may be assumed to reside either in separate atoms and molecules, or in a fluid medium caused to undu-

late. A special rate of vibration or pulsation originally imparted to a portion of the fluid medium enlivens that portion of matter with an individual existence, and constitutes it a distinct substance or element.

With respect to the different states of gas, liquid, and solid, it may be observed that there is no real incompatibility with each other in these physical conditions. They are often found together in the same substance. The liquid and the solid conditions supervene upon the gaseous condition rather than supersede it. Gay-Lussac made the remarkable observation that the vapours emitted by ice and water, both at 0° C., are of exactly equal tension. The passage from the liquid to the solid state is not made apparent in the volatility of water. The liquid and solid conditions do not appear as the extinction or suppression of the gaseous condition, but something *superadded* to that condition. The three conditions (or constitutions) probably always coexist in every liquid or solid substance, but one predominates over the others. In the general properties of matter we have, indeed, to include still further (1) the remarkable loss of elasticity in vapours under great pressure, which is distinguished by Mr. Faraday as the Cagnard Latour state, after the name of its discoverer, and is now undergoing an investigation by Dr. Andrews, which may be expected to throw much light upon its nature; (2) the colloidal condition or constitution, which intervenes between the liquid and crystalline states, extending into both and affecting probably all kinds of solid and liquid matter in a greater or less degree. The predominance of a certain physical state in a substance appears to be a distinction of a kind with those distinctions recognized in natural history as being produced by unequal development. Liquefaction or solidification, therefore, may not involve the suppression of either the atomic or the molecular movement, but only the restriction of its range. The hypothesis of atomic movement has been elsewhere assumed, irrespective of the gaseous condition, and is applied by Dr. Williamson to the elucidation of a remarkable class of chemical reactions which have their seat in a mixed liquid.

Lastly, molecular or diffusive mobility has an obvious bearing upon the communication of heat to gases by contact with liquid or solid surfaces. The impact of the gaseous molecule upon a surface possessing a different temperature, appears to be the condition for the transference of heat, or the heat movement, from one to the other. The more rapid the molecular movement of the gas, the more frequent the contact, with consequent communication of heat. Hence, probably, the great cooling-power of hydrogen gas as compared with air or oxygen. The gases named have the same specific heat for equal volumes; but

a hot object placed in hydrogen is really *touched* 3·8 times as frequently as it would be if placed in air, and 4 times as frequently as it would be if placed in an atmosphere of oxygen gas. Dalton had already ascribed this peculiarity of hydrogen to the high "mobility" of that gas. The same molecular property of hydrogen recommends the application of that gas in the air-engine, where the object is to alternately heat and cool a confined volume of gas with rapidity.

MOLECULES*

AN atom is a body which cannot be cut in two. A molecule is the smallest possible portion of a particular substance. No one has ever seen or handled a single molecule. Molecular science, therefore, is one of those branches of study which deal with things invisible and imperceptible by our senses, and which cannot be subjected to direct experiment.

The mind of man has perplexed itself with many hard questions. Is space infinite, and if so in what sense? Is the material world infinite in extent, and are all places within that extent equally full of matter? Do atoms exist, or is matter infinitely divisible?

The discussion of questions of this kind has been going on ever since men began to reason, and to each of us, as soon as we obtain the use of our faculties, the same old questions arise as fresh as ever. They form as essential a part of the science of the nineteenth century of our era, as of that of the fifth century before it.

We do not know much about the science organisation of Thrace twenty-two centuries ago, or of the machinery then employed for diffusing an interest in physical research. There were men, however, in those days, who devoted their lives to the pursuit of knowledge with an ardour worthy of the most distinguished members of the British Association; and the lectures in which Democritus explained the atomic theory to his fellow-citizens of Abdera realised, not in golden opinions only, but in golden talents, a sum hardly equalled even in America.

To another very eminent philosopher, Anaxagoras, best known to the world as the teacher of Socrates, we are indebted for the most important service to the atomic theory, which, after its statement by Democritus, remained to be done. Anaxagoras, in fact, stated a theory which so exactly contradicts the atomic theory of Democritus that the truth or falsehood of the one theory implies the falsehood or truth of the other. The question of the existence or non-existence of atoms cannot be presented to us this evening with greater clearness than in the alternative theories of these two philosophers.

Take any portion of matter, say a drop of water, and observe its properties. Like every other portion of matter we have ever seen, it is divisible. Divide it in two, each portion appears to retain all the properties of the original drop, and among others that of being divisible. The parts are similar to the whole in every respect except in absolute size.

Now go on repeating the process of division till the separate portions of water are so small that we can no longer perceive or handle them. Still we have no doubt that the sub-division might be carried further, if our senses were more acute and our instruments more delicate. Thus far all are agreed, but now the question arises, Can this sub-division be repeated for ever?

According to Democritus and the atomic school, we must answer in the negative. After a certain number of sub-divisions, the drop would be divided into a number of parts each of which is incapable of further sub-division. We should thus, in imagination, arrive at the atom, which, as its name literally signifies, cannot be cut in two. This is the atomic doctrine of Democritus, Epicurus, and Lucretius, and, I may add, of your lecturer.

According to Anaxagoras, on the other hand, the parts into which the drop is divided, are in all respects similar to the whole drop, the mere size of a body counting for nothing as regards the nature of its substance. Hence if the whole drop is divisible, so are its parts down to the minutest sub-divisions, and that without end.

The essence of the doctrine of Anaxagoras is that the parts of a body are in all respects similar to the whole. It was therefore called the doctrine of Homoiomereia. Anaxagoras did not of course assert this of the parts of organised bodies such as men and animals, but he maintained that those inorganic substances which appear to us homogeneous are really so, and that the universal experience of mankind testifies that every material body, without exception, is divisible.

The doctrine of atoms and that of homogeneity are thus in direct contradiction.

But we must now go on to molecules. Molecule is a modern word. It does not occur in *Johnson's Dictionary*. The ideas it embodies are those belonging to modern chemistry.

A drop of water, to return to our former example, may be divided into a certain number, and no more, of portions similar

to each other. Each of these the modern chemist calls a molecule of water. But it is by no means an atom, for it contains two different substances, oxygen and hydrogen, and by a certain process the molecule may be actually divided into two parts, one consisting of oxygen and the other of hydrogen. According to the received doctrine, in each molecule of water there are two molecules of hydrogen and one of oxygen. Whether these are or are not ultimate atoms I shall not attempt to decide.

We now see what a molecule is, as distinguished from an atom.

A molecule of a substance is a small body such that if, on the one hand, a number of similar molecules were assembled together they would form a mass of that substance, while on the other hand, if any portion of this molecule were removed, it would no longer be able, along with an assemblage of other molecules similarly treated, to make up a mass of the original substance.

Every substance, simple or compound, has its own molecule. If this molecule be divided, its parts are molecules of a different substance or substances from that of which the whole is a molecule. An atom, if there is such a thing, must be a molecule of an elementary substance. Since, therefore, every molecule is not an atom, but every atom is a molecule, I shall use the word molecule as the more general term.

I have no intention of taking up your time by expounding the doctrines of modern chemistry with respect to the molecules of different substances. It is not the special but the universal interest of molecular science which encourages me to address you. It is not because we happen to be chemists or physicists or specialists of any kind that we are attracted towards this centre of all material existence, but because we all belong to a race endowed with faculties which urge us on to search deep and ever deeper into the nature of things.

We find that now, as in the days of the earliest physical speculations, all physical researches appear to converge towards the same point, and every inquirer, as he looks forward into the dim region towards which the path of discovery is leading him, sees, each according to his sight, the vision of the same quest.

One may see the atom as a material point, invested and surrounded by potential forces. Another sees no garment of force, but only the bare and utter hardness of mere impenetrability.

But though many a speculator, as he has seen the vision recede before him into the innermost sanctuary of the inconceivably little, has had to confess that the quest was not for him, and though philosophers in every age have been exhorting each other to direct their minds to some more useful and attainable aim, each generation, from the earliest dawn of science to the present time, has contributed a due proportion of its ablest intellects to the quest of the ultimate atom.

Our business this evening is to describe some researches in molecular science, and in particular to place before you any definite information which has been obtained respecting the molecules themselves. The old atomic theory, as described by Lucretius and revived in modern times, asserts that the molecules of all bodies are in motion, even when the body itself appears to be at rest. These motions of molecules are in the case of solid bodies confined within so narrow a range that even with our best microscopes we cannot detect that they alter their places at all. In liquids and gases, however, the molecules are not confined within any definite limits, but work their way through the whole mass, even when that mass is not disturbed by any visible motion.

This process of diffusion, as it is called, which goes on in gases and liquids and even in some solids, can be subjected to experiment, and forms one of the most convincing proofs of the motion of molecules.

Now the recent progress of molecular science began with the study of the mechanical effect of the impact of these moving molecules when they strike against any solid body. Of course these flying molecules must beat against whatever is placed among them, and the constant succession of these strokes is, according to our theory, the sole cause of what is called the pressure of air and other gases.

This appears to have been first suspected by Daniel Bernoulli, but he had not the means which we now have of verifying the theory. The same theory was afterwards brought forward independently by Lesage, of Geneva, who, however, devoted most of his labour to the explanation of gravitation by the impact of atoms. Then Herapath, in his "Mathematical Physics,"

* Lecture delivered before the British Association at Bradford, by Prof. Clerk-Maxwell, F.R.S.

published in 1847, made a much more extensive application of the theory to gases, and Dr. Joule, whose absence from our meeting we must all regret, calculated the actual velocity of the molecules of hydrogen.

The further development of the theory is generally supposed to have been begun with a paper by Krönig, which does not, however, so far as I can see, contain any improvement on what had gone before. It seems, however, to have drawn the attention of Prof. Clausius to the subject, and to him we owe a very large part of what has been since accomplished.

We all know that air or any other gas placed in a vessel presses against the sides of the vessel, and against the surface of any body placed within it. On the kinetic theory this pressure is entirely due to the molecules striking against these surfaces, and thereby communicating to them a series of impulses which follow each other in such rapid succession that they produce an effect which cannot be distinguished from that of a continuous pressure.

If the velocity of the molecules is given, and the number varied, then since each molecule, on an average, strikes the side of the vessel the same number of times, and with an impulse of the same magnitude, each will contribute an equal share to the whole pressure. The pressure in a vessel of given size is therefore proportional to the number of molecules in it, that is to the quantity of gas in it.

This is the complete dynamical explanation of the fact discovered by Robert Boyle, that the pressure of air is proportional to its density. It shows also that of different portions of gas forced into a vessel, each produces its own part of the pressure independently of the rest, and this whether these portions be of the same gas or not.

Let us next suppose that the velocity of the molecules is increased. Each molecule will now strike the sides of the vessel a greater number of times in a second, but besides this, the impulse of each blow will be increased in the same proportion, so that the part of the pressure due to each molecule will vary as the *square* of the velocity. Now the increase of the square of velocity corresponds, in our theory, to a rise of temperature, and in this way we can explain the effect of warming the gas, and also the law discovered by Charles that the proportional expansion of all gases between given temperatures is the same.

The dynamical theory also tells us what will happen if molecules of different masses are allowed to knock about together. The greater masses will go slower than the smaller ones, so that, on an average, every molecule, great or small, will have the same energy of motion.

The proof of this dynamical theorem, in which I claim the priority, has recently been greatly developed and improved by Dr. Ludwig Boltzmann. The most important consequence which flows from it is that a cubic centimetre of every gas at standard temperature and pressure contains the same number of molecules. This is the dynamical explanation of Gay Lussac's law of the equivalent volumes of gases. But we must now descend to particulars, and calculate the actual velocity of a molecule of hydrogen.

A cubic centimetre of hydrogen, at the temperature of melting ice and at a pressure of one atmosphere, weighs 0.00008954 grammes. We have to find at what rate this small mass must move (whether altogether or in separate molecules makes no difference) so as to produce the observed pressure on the sides of the cubic centimetre. This is the calculation which was first made by Dr. Joule, and the result is 1,859 metres per second. This is what we are accustomed to call a great velocity. It is greater than any velocity obtained in artillery practice. The velocity of other gases is less, as you will see by the table, but in all cases it is very great as compared with that of bullets.

We have now to conceive the molecules of the air in this hall flying about in all directions, at a rate of about seventeen miles in a minute.

If all these molecules were flying in the same direction, they would constitute a wind blowing at the rate of seventeen miles a minute, and the only wind which approaches this velocity is that which proceeds from the mouth of a cannon. How, then, are you and I able to stand here? Only because the molecules happen to be flying in different directions, so that those which strike against our backs enable us to support the storm which is beating against our faces. Indeed, if this molecular bombardment were to cease, even for an instant, our veins would swell, our breath would leave us, and we should, literally, expire. But

it is not only against us or against the walls of the room that the molecules are striking. Consider the immense number of them, and the fact that they are flying in every possible direction, and you will see that they cannot avoid striking each other. Every time that two molecules come into collision, the paths of both are changed, and they go off in new directions. Thus each molecule is continually getting its course altered, so that in spite of its great velocity it may be a long time before it reaches any great distance from the point at which it set out.

I have here a bottle containing ammonia. Ammonia is a gas which you can recognise by its smell. Its molecules have a velocity of six hundred metres per second, so that if their course had not been interrupted by striking against the molecules of air in the hall, everyone in the most distant gallery would have smelt ammonia before I was able to pronounce the name of the gas. But instead of this, each molecule of ammonia is so jostled about by the molecules of air, that it is sometimes going one way and sometimes another. It is like a hare which is always doubling, and though it goes a great pace, it makes very little progress. Nevertheless, the smell of ammonia is now beginning to be perceptible at some distance from the bottle. The gas does diffuse itself through the air, though the process is a slow one, and if we could close up every opening of this hall so as to make it air-tight, and leave everything to itself for some weeks, the ammonia would become uniformly mixed through every part of the air in the hall.

This property of gases, that they diffuse through each other, was first remarked by Priestley. Dalton showed that it takes place quite independently of any chemical action between the inter-diffusing gases. Graham, whose researches were especially directed towards those phenomena which seem to throw light on molecular motions, made a careful study of diffusion, and obtained the first results from which the rate of diffusion can be calculated.

Still more recently the rates of diffusion of gases into each other have been measured with great precision by Prof. Loschmidt of Vienna.

He placed the two gases in two similar vertical tubes, the lighter gas being placed above the heavier, so as to avoid the formation of currents. He then opened a sliding valve, so as to make the two tubes into one, and after leaving the gases to themselves for an hour or so, he shut the valve, and determined how much of each gas had diffused into the other.

As most gases are invisible, I shall exhibit gaseous diffusion to you by means of two gases, ammonia and hydrochloric acid, which, when they meet, form a solid product. The ammonia, being the lighter gas, is placed above the hydrochloric acid, with a stratum of air between, but you will soon see that the gases can diffuse through this stratum of air, and produce a cloud of white smoke when they meet. During the whole of this process no currents or any other visible motion can be detected. Every part of the vessel appears as calm as a jar of undisturbed air.

But, according to our theory, the same kind of motion is going on in calm air as in the inter-diffusing gases, the only difference being that we can trace the molecules from one place to another more easily when they are of a different nature from those through which they are diffusing.

If we wish to form a mental representation of what is going on among the molecules in calm air, we cannot do better than observe a swarm of bees, when every individual bee is flying furiously, first in one direction, and then in another, while the swarm, as a whole, either remains at rest, or sails slowly through the air.

In certain seasons, swarms of bees are apt to fly off to a great distance, and the owners, in order to identify their property when they find them on other people's ground, sometimes throw handfuls of flour at the swarm. Now let us suppose that the flour thrown at the flying swarm has whitened those bees only which happened to be in the lower half of the swarm, leaving those in the upper half free from flour.

If the bees still go on flying hither and thither in an irregular manner, the floury bees will be found in continually increasing proportions in the upper part of the swarm, till they have become equally diffused through every part of it. But the reason of this diffusion is not because the bees were marked with flour, but because they are flying about. The only effect of the marking is to enable us to identify certain bees.

We have no means of marking a select number of molecules of air, so as to trace them after they have become diffused among

others, but we may communicate to them some property by which we may obtain evidence of their diffusion.

For instance, if a horizontal stratum of air is moving horizontally, molecules diffusing out of this stratum into those above and below will carry their horizontal motion with them, and so tend to communicate motion to the neighbouring strata, while molecules diffusing out of the neighbouring strata into the moving one will tend to bring it to rest. The action between the strata is somewhat like that of two rough surfaces, one of which slides over the other, rubbing on it. Friction is the name given to this action between solid bodies; in the case of fluids it is called internal friction or viscosity.

It is in fact only another kind of diffusion—a lateral diffusion of momentum, and its amount can be calculated from data derived from observations of the first kind of diffusion, that of matter. The comparative values of the viscosity of different gases were determined by Graham in his researches on the transpiration of gases through long narrow tubes, and their absolute values have been deduced from experiments on the oscillation of discs by Oscar Meyer and myself.

Another way of tracing the diffusion of molecules through calm air is to heat the upper stratum of the air in a vessel, and so observe the rate at which this heat is communicated to the lower strata. This, in fact, is a third kind of diffusion—that of energy, and the rate at which it must take place was calculated from data derived from experiments on viscosity before any direct experiments on the conduction of heat had been made. Prof. Stefan, of Vienna, has recently, by a very delicate method, succeeded in determining the conductivity of air, and he finds it, as he tells us, in striking agreement with the value predicted by the theory.

All these three kinds of diffusion—the diffusion of matter, of momentum, and of energy—are carried on by the motion of the molecules. The greater the velocity of the molecules and the farther they travel before their paths are altered by collision with other molecules, the more rapid will be the diffusion. Now we know already the velocity of the molecules, and therefore by experiments on diffusion we can determine how far, on an average, a molecule travels without striking another. Prof. Clausius, of Bonn, who first gave us precise ideas about the motion of agitation of molecules, calls this distance the mean path of a molecule. I have calculated, from Prof. Loschmidt's diffusion experiments, the mean path of the molecules of four well-known gases. The average distance travelled by a molecule between one collision and another is given in the table. It is a very small distance, quite imperceptible to us even with our best microscopes. Roughly speaking, it is about the tenth part of the length of a wave of light, which you know is a very small quantity. Of course the time spent on so short a path by such swift molecules must be very small. I have calculated the number of collisions which each must undergo in a second. They are given in the table and are reckoned by thousands of millions. No wonder that the travelling power of the swiftest molecule is but small, when its course is completely changed thousands of millions of times in a second.

The three kinds of diffusion also take place in liquids, but the relation between the rates at which they take place is not so simple as in the case of gases. The dynamical theory of liquids is not so well understood as that of gases, but the principal difference between a gas and a liquid seems to be that in a gas each molecule spends the greater part of its time in describing its free path, and is for a very small portion of its time engaged in encounters with other molecules, whereas in a liquid the molecule has hardly any free path, and is always in a state of close encounter with other molecules.

Hence in a liquid the diffusion of motion from one molecule to another takes place much more rapidly than the diffusion of the molecules themselves, for the same reason that it is more expeditious in a dense crowd to pass on a letter from hand to hand than to give it to a special messenger to work his way through the crowd. I have here a jar, the lower part of which contains a solution of copper sulphate, while the upper part contains pure water. It has been standing here since Friday, and you see how little progress the blue liquid has made in diffusing itself through the water above. The rate of diffusion of a solution of sugar has been carefully observed by Voit. Comparing his results with those of Loschmidt on gases, we find that about as much diffusion takes place in a second in gases as requires a day in liquids.

The rate of diffusion of momentum is also slower in liquids

than in gases, but by no means in the same proportion. The same amount of motion takes about ten times as long to subside in water as in air, as you will see by what takes place when I stir these two jars, one containing water and the other air. There is still less difference between the rates at which a rise of temperature is propagated through a liquid and through a gas.

In solids the molecules are still in motion, but their motions are confined within very narrow limits. Hence the diffusion of matter does not take place in solid bodies, though that of motion and heat takes place very freely. Nevertheless, certain liquids can diffuse through colloid solids, such as jelly and gum, and hydrogen can make its way through iron and palladium.

We have no time to do more than mention that most wonderful molecular motion which is called electrolysis. Here is an electric current passing through acidulated water, and causing oxygen to appear at one electrode and hydrogen at the other. In the space between, the water is perfectly calm, and yet two opposite currents of oxygen and of hydrogen must be passing through it. The physical theory of this process has been studied by Clausius, who has given reasons for asserting that in ordinary water the molecules are not only moving, but every now and then striking each other with such violence that the oxygen and hydrogen of the molecules part company, and dance about through the crowd, seeking partners which have become dissociated in the same way. In ordinary water these exchanges produce, on the whole, no observable effect, but no sooner does the electromotive force begin to act than it exerts its guiding influence on the unattached molecules, and bends the course of each toward its proper electrode, till the moment when, meeting with an unappropriated molecule of the opposite kind, it enters again into a more or less permanent union with it till it is again dissociated by another shock. Electrolysis, therefore, is a kind of diffusion assisted by electromotive force.

Another branch of molecular science is that which relates to the exchange of molecules between a liquid and a gas. It includes the theory of evaporation and condensation, in which the gas in question is the vapour of the liquid, and a so the theory of the absorption of a gas by a liquid of a different substance. The researches of Dr. Andrews on the relations between the liquid and the gaseous state have shown us that though the statements in our own elementary text-books may be so neatly expressed that they appear almost self-evident, their true interpretation may involve some principle so profound that, till the right man has laid hold of it, no one ever suspects that anything is left to be discovered.

These, then, are, some of the fields from which the data of molecular science are gathered. We may divide the ultimate results into three ranks, according to the completeness of our knowledge of them.

To the first rank belong the relative masses of the molecules of different gases, and their velocities in metres per second. These data are obtained from experiments on the pressure and density of gases, and are known to a high degree of precision.

In the second rank we must place the relative size of the molecules of different gases, the length of their mean paths, and the number of collisions in a second. These quantities are deduced from experiments on the three kinds of diffusion. Their received values must be regarded as rough approximations till the methods of experimenting are greatly improved.

There is another set of quantities which we must place in the third rank, because our knowledge of them is neither precise, as in the first rank, nor approximate, as in the second, but is only as yet of the nature of a probable conjecture. These are the absolute mass of a molecule, its absolute diameter, and the number of molecules in a cubic centimetre. We know the relative masses of different molecules with great accuracy, and we know their relative diameters approximately. From these we can deduce the relative densities of the molecules themselves. So far we are on firm ground.

The great resistance of liquids to compression makes it probable that their molecules must be at about the same distance from each other as that at which two molecules of the same substance in the gaseous form act on each other during an encounter. This conjecture has been put to the test by Lorenz Meyer, who has compared the densities of different liquids with the calculated relative densities of the molecules of their vapours, and has found a remarkable correspondence between them.

Now Loschmidt has deduced from the dynamical theory the

following remarkable proportion :—As the volume of a gas is to the combined volume of all the molecules contained in it, so is the mean path of a molecule to one-eighth of the diameter of a molecule.

Assuming that the volume of the substance, when reduced to the liquid form, is not much greater than the combined volume of the molecules, we obtain from this proportion the diameter of a molecule. In this way Loschmidt, in 1865, made the first estimate of the diameter of a molecule. Independently of him and of each other, Mr. Stoney in 1868, and Sir W. Thomson in 1870, published results of a similar kind, those of Thomson being deduced not only in this way, but from considerations derived from the thickness of soap bubbles, and from the electric properties of metals.

According to the table, which I have calculated from Loschmidt's data, the size of the molecules of hydrogen is such that about two million of them in a row would occupy a millimetre, and a million million million million of them would weigh between four and five grammes.

In a cubic centimetre of any gas at standard pressure and temperature there are about nineteen million million molecules. All these numbers of the third rank are, I need not tell you, to be regarded as at present conjectural. In order to warrant us in putting any confidence in numbers obtained in this way, we should have to compare together a greater number of independent data than we have as yet obtained, and to show that they lead to consistent results.

Thus far we have been considering molecular science as an inquiry into natural phenomena. But though the professed aim of all scientific work is to unravel the secrets of nature, it has another effect, not less valuable, on the mind of the worker. It leaves him in possession of methods which nothing but scientific work could have led him to invent, and it places him in a position from which many regions of nature, besides that which he has been studying, appear under a new aspect.

The study of molecules has developed a method of its own, and it has also opened up new views of nature.

When Lucretius wishes us to form a mental representation of the motion of atoms, he tells us to look at a sunbeam shining through a darkened room (the same instrument of research by which Dr. Tyndall makes visible to us the dust we breathe,) and to observe the motes which chase each other in all directions through it. This motion of the visible motes, he tells us, is but a result of the far more complicated motion of the invisible atoms which knock the motes about. In his dream of nature, as Tennyson tells us, he

"saw the flaring atom-streams
And torrents of her myriad universe,
Ruining along the illimitable inane,
Fly on to clash together again, and make
Another and another frame of things
For ever."

And it is no wonder that he should have attempted to burst the bonds of Fate by making his atoms deviate from their courses at quite uncertain times and places, thus attributing to them a kind of irrational free will, which on his materialistic theory is the only explanation of that power of voluntary action of which we ourselves are conscious.

As long as we have to deal with only two molecules, and have all the data given us, we can calculate the result of their encounter, but when we have to deal with millions of molecules, each of which has millions of encounters in a second, the complexity of the problem seems to shut out all hope of a legitimate solution.

The modern atomists have therefore adopted a method which is I believe new in the department of mathematical physics, though it has long been in use in the Section of Statistics. When the working members of Section F get hold of a Report of the Census, or any other document containing the numerical data of Economic and Social Science, they begin by distributing the whole population into groups, according to age, income-tax, education, religious belief, or criminal convictions. The number of individuals is far too great to allow of their tracing the history of each separately, so that, in order to reduce their labour within human limits, they concentrate their attention on a small number of artificial groups. The varying number of individuals in each group, and not the varying state of each individual, is the primary datum from which they work.

This, of course, is not the only method of studying human nature. We may observe the conduct of individual men and compare it with that conduct which their previous character and their present circumstances, according to the best existing theory,

would lead us to expect. Those who practise this method endeavour to improve their knowledge of the elements of human nature, in much the same way as an astronomer corrects the elements of a planet by comparing its actual position with that deduced from the received elements. The study of human nature by parents and schoolmasters, by historians and statesmen, is therefore to be distinguished from that carried on by registrars and tabulators, and by those statesmen who put their faith in figures. The one may be called the historical, and the other the statistical method.

The equations of dynamics completely express the laws of the historical method as applied to matter, but the application of these equations implies a perfect knowledge of all the data. But the smallest portion of matter which we can subject to experiment consists of millions of molecules, not one of which ever becomes individually sensible to us. We cannot, therefore, ascertain the actual motion of any one of these molecules, so that we are obliged to abandon the strict historical method, and to adopt the statistical method of dealing with large groups of molecules.

The data of the statistical method as applied to molecular science are the sums of large numbers of molecular quantities. In studying the relations between quantities of this kind, we meet with a new kind of regularity, the regularity of averages, which we can depend upon quite sufficiently for all practical purposes, but which can make no claim to that character of absolute precision which belongs to the laws of abstract dynamics.

Thus molecular science teaches us that our experiments can never give us anything more than statistical information, and that no law deduced from them can pretend to absolute precision. But when we pass from the contemplation of our experiments to that of the molecules themselves, we leave the world of chance and change, and enter a region where everything is certain and immutable.

The molecules are conformed to a constant type with a precision which is not to be found in the sensible properties of the bodies which they constitute. In the first place the mass of each individual molecule, and all its other properties, are absolutely unalterable. In the second place the properties of all molecules of the same kind are absolutely identical.

Let us consider the properties of two kinds of molecules, those of oxygen and those of hydrogen.

We can procure specimens of oxygen from very different sources—from the air, from water, from rocks of every geological epoch. The history of these specimens has been very different, and if, during thousands of years, difference of circumstances could produce difference of properties, these specimens of oxygen would show it.

In like manner we may procure hydrogen from water, from coal, or, as Graham did, from meteoric iron. Take two litres of any specimen of hydrogen, it will combine with exactly one litre of any specimen of oxygen, and will form exactly two litres of the vapour of water.

Now if, during the whole previous history of either specimen, whether imprisoned in the rocks, flowing in the sea, or careering through unknown regions with the meteorites, any modification of the molecules had taken place, these relations would no longer be preserved.

But we have another and an entirely different method of comparing the properties of molecules. The molecule, though indestructible, is not a hard rigid body, but is capable of internal movements, and when these are excited it emits rays, the wave-length of which is a measure of the time of vibration of the molecule.

By means of the spectroscope the wave-lengths of different kinds of light may be compared to within one ten-thousandth part. In this way it has been ascertained, not only that molecules taken from every specimen of hydrogen in our laboratories have the same set of periods of vibration, but that light, having the same set of periods of vibration, is emitted from the sun and from the fixed stars.

We are thus assured that molecules of the same nature as those of our hydrogen exist in those distant regions, or at least did exist when the light by which we see them was emitted.

From a comparison of the dimensions of the buildings of the Egyptians with those of the Greeks, it appears that they have a common measure. Hence, even if no ancient author had recorded the fact that the two nations employed the same cubit as a standard of length, we might prove it from the buildings themselves. We should also be justified in asserting that at some time or other a material standard of length must have been

carried from one country to the other, or that both countries had obtained their standards from a common source.

But in the heavens we discover by their light, and by their light alone, stars so distant from each other that no material thing can ever have passed from one to another, and yet this light, which is to us the sole evidence of the existence of these distant worlds, tells us also that each of them is built up of molecules of the same kinds as those which we find on earth. A molecule of hydrogen, for example, whether in Sirius or in Arcturus, executes its vibrations in precisely the same time.

Each molecule, therefore, throughout the universe, bears impressed on it the stamp of a metric system as distinctly as does the metre of the Archives at Paris, or the double royal cubit of the Temple of Karnac.

No theory of evolution can be formed to account for the similarity of molecules, for evolution necessarily implies continuous change, and the molecule is incapable of growth or decay, of generation or destruction.

None of the processes of Nature, since the time when Nature began, have produced the slightest difference in the properties of any molecule. We are therefore unable to ascribe either the existence of the molecules or the identity of their properties to the operation of any of the causes which we call natural.

On the other hand, the exact quality of each molecule to all others of the same kind gives it, as Sir John Herschel has well said, the essential character of a manufactured article, and precludes the idea of its being eternal and self-existent.

Thus we have been led, along a strictly scientific path, very near to the point at which Science must stop. Not that Science is debarred from studying the internal mechanism of a molecule which she cannot take to pieces, any more than from investigating an organism which she cannot put together. But in tracing back the history of matter Science is arrested when she assures herself, on the one hand, that the molecule has been made, and on the other that it has not been made by any of the processes we call natural.

Science is incompetent to reason upon the creation of matter itself out of nothing. We have reached the utmost limit of our thinking faculties when we have admitted that because matter cannot be eternal and self-existent it must have been created.

It is only when we contemplate, not matter in itself, but the form in which it actually exists, that our mind finds something on which it can lay hold.

That matter, as such, should have certain fundamental properties—that it should exist in space and be capable of motion, that its motion should be persistent, and so on, are truths which may, for anything we know, be of the kind which metaphysicians call necessary. We may use our knowledge of such truths for purposes of deduction but we have no data for speculating as to their origin.

But that there should be exactly so much matter and no more in every molecule of hydrogen is a fact of a very different order. We have here a particular distribution of matter—a *collocation*—to use the expression of Dr. Chalmers, of things which we have no difficulty in imagining to have been arranged otherwise.

The form and dimensions of the orbits of the planets, for instance, are not determined by any law of nature, but depend upon a particular collocation of matter. The same is the case with respect to the size of the earth, from which the standard of what is called the metrical system has been derived. But these astronomical and terrestrial magnitudes are far inferior in scientific importance to that most fundamental of all standards which forms the base of the molecular system. Natural causes, as we know, are at work, which tend to modify, if they do not at length destroy, all the arrangements and dimensions of the earth and the whole solar system. But though in the course of ages catastrophes have occurred and may yet occur in the heavens, though ancient systems may be dissolved and new systems evolved out of their ruins, the molecules out of which these systems are built—the foundation stones of the material universe—remain unbroken and unworn.

They continue this day as they were created, perfect in number and measure and weight, and from the ineffaceable characters impressed on them we may learn that those aspirations after accuracy in measurement, truth in statement, and justice in action, which we reckon among our noblest attributes as men, are ours because they are essential constituents of the image of Him Who in the beginning created, not only the heaven and the earth, but the materials of which heaven and earth consist.

Table of Molecular Data.

		Hydrogen.	Oxygen.	Carbonic oxide.	Carbonic acid.
Rank	Mass of molecule (hydrogen = 1)	1	16	14	22
I.	Velocity (of mean square), metres per second at 0° C.	1859	465	497	396
	Mean path, tenth-metres.	965	560	482	379
Rank II.	Collisions in a second, (millions)	17750	7646	9489	9720
	Diameter, tenth-metre	5.8	7.6	8.3	9.3
Rank III.	Mass, twenty-fifth-grammes.	46	736	644	1012

Table of Diffusion: (centimetre)² second measure.

	Calculated	Observed.	
H & O	0.7086	0.7214	Diffusion of matter observed by Loschmidt.
H & CO	0.6519	0.6422	
H & CO ₂	0.5575	0.5558	
O & CO	0.1807	0.1802	
O & CO ₂	0.1427	0.1409	
CO & CO ₂	0.1386	0.1406	Diffusion of momentum Graham and Meyer.
H	1.2990	1.49	
O	0.1884	0.213	
CO	0.1748	0.212	Diffusion of temperature observed by Stefan.
CO ₂	0.1087	0.117	
Air		0.256	
Copper		1.077	
Iron		0.183	
Cane sugar in water		0.00000365	Voit.
Diffusion in a day		0.3144	
Salt in water . .		0.00000116	Flick.

A T O M

A TOM (*ἄτομος*) is a body which cannot be cut in two. The atomic theory is a theory of the constitution of bodies, which asserts that they are made up of atoms. The opposite theory is that of the homogeneity and continuity of bodies, and asserts, at least in the case of bodies having no apparent organisation, such, for instance, as water, that as we can divide a drop of water into two parts which are each of them drops of water, so we have reason to believe that these smaller drops can be divided again, and the theory goes on to assert that there is nothing in the nature of things to hinder this process of division from being repeated over and over again, times without end. This is the doctrine of the infinite divisibility of bodies, and it is in direct contradiction with the theory of atoms.

The atomists assert that after a certain number of such divisions the parts would be no longer divisible, because each of them would be an atom. The advocates of the

continuity of matter assert that the smallest conceivable body has parts, and that whatever has parts may be divided.

In ancient times Democritus was the founder of the atomic theory, while Anaxagoras propounded that of continuity, under the name of the doctrine of homœomeria (*ὁμοιομέρεια*), or of the similarity of the parts of a body to the whole. The arguments of the atomists, and their replies to the objections of Anaxagoras, are to be found in Lucretius.

In modern times the study of nature has brought to light many properties of bodies which appear to depend on the magnitude and motions of their ultimate constituents, and the question of the existence of atoms has once more become conspicuous among scientific inquiries.

We shall begin by stating the opposing doctrines of atoms and of continuity before giving an outline of the state of

molecular science as it now exists. In the earliest times the most ancient philosophers whose speculations are known to us seem to have discussed the ideas of number and of continuous magnitude, of space and time, of matter and motion, with a native power of thought which has probably never been surpassed. Their actual knowledge, however, and their scientific experience were necessarily limited, because in their days the records of human thought were only beginning to accumulate. It is probable that the first exact notions of quantity were founded on the consideration of number. It is by the help of numbers that concrete quantities are practically measured and calculated. Now, number is discontinuous. We pass from one number to the next *per saltum*. The magnitudes, on the other hand, which we meet with in geometry, are essentially continuous. The attempt to apply numerical methods to the comparison of geometrical quantities led to the doctrine of incommensurables, and to that of the infinite divisibility of space. Meanwhile, the same considerations had not been applied to time, so that in the days of Zeno of Elea time was still regarded as made up of a finite number of "moments," while space was confessed to be divisible without limit. This was the state of opinion when the celebrated arguments against the possibility of motion, of which that of Achilles and the tortoise is a specimen, were propounded by Zeno, and such, apparently, continued to be the state of opinion till Aristotle pointed out that time is divisible without limit, in precisely the same sense that space is. And the slowness of the development of scientific ideas may be estimated from the fact that Bayle does not see any force in this statement of Aristotle, but continues to admire the paradox of Zeno. (Bayle's *Dictionary*, art. "Zeno"). Thus the direction of true scientific progress was for many ages towards the recognition of the infinite divisibility of space and time.

It was easy to attempt to apply similar arguments to matter. If matter is extended and fills space, the same mental operation by which we recognise the divisibility of space may be applied, in imagination at least, to the matter which occupies space. From this point of view the atomic doctrine might be regarded as a relic of the old numerical way of conceiving magnitude, and the opposite doctrine of the infinite divisibility of matter might appear for a time the most scientific. The atomists, on the other hand, asserted very strongly the distinction between matter and space. The atoms, they said, do not fill up the universe; there are void spaces between them. If it were not so, Lucretius tells us, there could be no motion, for the atom which gives way first must have some empty place to move into.

"Quapropter locus est intactus, inane, vacansque
Quod si non esset, nulla ratione moveri
Res possent; namque, officium quod corporis exstat,
Officere atque obstande, id in omni tempore adesset
Omnibus: haud igitur quicquam procedere posset,
Principium quoniam cedendi nulla daret res."

—*De Rerum Natura*, i. 335.

The opposite school maintained then, as they have always done, that there is no vacuum—that every part of space is full of matter, that there is a universal plenum, and that all motion is like that of a fish in the water, which yields in front of the fish because the fish leaves room for it behind.

"Cedere squamigeris latice nitentibus aiunt
Et liquidas aperire vias, quia post loca pisces
Linquant, quo possint cedentes confluere undae."

—i. 373.

In modern times Descartes held that, as it is of the essence of matter to be extended in length, breadth, and thickness, so it is of the essence of extension to be occu-

pied by matter, for extension cannot be an extension of nothing.

"Ac proinde si quaeratur quid fiet, si Deus auferat omne corpus quod in aliquo vase continetur, et nullum aliud in ablato locum venire permittat? respondendum est, vasis latera sibi invicem hoc ipso fore contigua. Cum enim inter duo corpora nihil interjacet, necesse est ut se mutuo tangant, ac manifeste repugnat ut distent, sive ut inter ipsa sit distantia, et tamen ut ista distantia sit nihil; quia omnis distantia est modus extensionis, et ideo sine substantia extensa esse non potest."—*Principia*, ii. 18.

This identification of extension with substance runs through the whole of Descartes's works, and it forms one of the ultimate foundations of the system of Spinoza. Descartes, consistently with this doctrine, denied the existence of atoms as parts of matter, which by their own nature are indivisible. He seems to admit, however, that the Deity might make certain particles of matter indivisible in this sense, that no creature should be able to divide them. These particles, however, would be still divisible by their own nature, because the Deity cannot diminish his own power, and therefore must retain his power of dividing them. Leibnitz, on the other hand, regarded his monad as the ultimate element of everything.

There are thus two modes of thinking about the constitution of bodies, which have had their adherents both in ancient and in modern times. They correspond to the two methods of regarding quantity—the arithmetical and the geometrical. To the atomist the true method of estimating the quantity of matter in a body is to count the atoms in it. The void spaces between the atoms count for nothing. To those who identify matter with extension, the volume of space occupied by a body is the only measure of the quantity of matter in it.

Of the different forms of the atomic theory, that of Boscovich may be taken as an example of the purest monadism. According to Boscovich matter is made up of atoms. Each atom is an indivisible point, having position in space, capable of motion in a continuous path, and possessing a certain mass, whereby a certain amount of force is required to produce a given change of motion. Besides this the atom is endowed with potential force, that is to say, that any two atoms attract or repel each other with a force depending on their distance apart. The law of this force, for all distances greater than say the thousandth of an inch, is an attraction varying as the inverse square of the distance. For smaller distances the force is an attraction for one distance and a repulsion for another, according to some law not yet discovered. Boscovich himself, in order to obviate the possibility of two atoms ever being in the same place, asserts that the ultimate force is a repulsion which increases without limit as the distance diminishes without limit, so that two atoms can never coincide. But this seems an unwarrantable concession to the vulgar opinion that two bodies cannot co-exist in the same place. This opinion is deduced from our experience of the behaviour of bodies of sensible size, but we have no experimental evidence that two atoms may not sometimes coincide. For instance, if oxygen and hydrogen combine to form water, we have no experimental evidence that the molecule of oxygen is not in the very same place with the two molecules of hydrogen. Many persons cannot get rid of the opinion that all matter is extended in length, breadth, and depth. This is a prejudice of the same kind with the last, arising from our experience of bodies consisting of immense multitudes of atoms. The system of atoms, according to Boscovich, occupies a certain region of space in virtue of the forces acting between the component atoms of the system and any other atoms when brought near them. No other system of atoms can occupy the same region of space at the same time, because, before it could do so, the mutual

action of the atoms would have caused a repulsion between the two systems insuperable by any force which we can command. Thus, a number of soldiers with firearms may occupy an extensive region to the exclusion of the enemy's armies, though the space filled by their bodies is but small. In this way Boscovich explained the apparent extension of bodies consisting of atoms, each of which is devoid of extension. According to Boscovich's theory, all action between bodies is action at a distance. There is no such thing in nature as actual contact between two bodies. When two bodies are said in ordinary language to be in contact, all that is meant is that they are so near together that the repulsion between the nearest pairs of atoms belonging to the two bodies is very great.

Thus, in Boscovich's theory, the atom has continuity of existence in time and space. At any instant of time it is at some point of space, and it is never in more than one place at a time. It passes from one place to another along a continuous path. It has a definite mass which cannot be increased or diminished. Atoms are endowed with the power of acting on one another by attraction or repulsion, the amount of the force depending on the distance between them. On the other hand, the atom itself has no parts or dimensions. In its geometrical aspect it is a mere geometrical point. It has no extension in space. It has not the so-called property of Impenetrability, for two atoms may exist in the same place. This we may regard as one extreme of the various opinions about the constitution of bodies.

The opposite extreme, that of Anaxagoras—the theory that bodies apparently homogeneous and continuous are so in reality—is, in its extreme form, a theory incapable of development. To explain the properties of any substance by this theory is impossible. We can only admit the observed properties of such substance as ultimate facts. There is a certain stage, however, of scientific progress in which a method corresponding to this theory is of service. In hydrostatics, for instance, we define a fluid by means of one of its known properties, and from this definition we make the system of deductions which constitutes the science of hydrostatics. In this way the science of hydrostatics may be built upon an experimental basis, without any consideration of the constitution of a fluid as to whether it is molecular or continuous. In like manner, after the French mathematicians had attempted, with more or less ingenuity, to construct a theory of elastic solids from the hypothesis that they consist of atoms in equilibrium under the action of their mutual forces, Stokes and others showed that all the results of this hypothesis, so far at least as they agreed with facts, might be deduced from the postulate that elastic bodies exist, and from the hypothesis that the smallest portions into which we can divide them are sensibly homogeneous. In this way the principle of continuity, which is the basis of the method of Fluxions and the whole of modern mathematics, may be applied to the analysis of problems connected with material bodies by assuming them, for the purpose of this analysis, to be homogeneous. All that is required to make the results applicable to the real case is that the smallest portions of the substance of which we take any notice shall be sensibly of the same kind. Thus, if a railway contractor has to make a tunnel through a hill of gravel, and if one cubic yard of the gravel is so like another cubic yard that for the purposes of the contract they may be taken as equivalent, then, in estimating the work required to remove the gravel from the tunnel, he may, without fear of error, make his calculations as if the gravel were a continuous substance. But if a worm has to make his way through the gravel, it makes the greatest possible difference to him whether he tries to push right against a piece of gravel, or directs his course through

one of the intervals between the pieces; to him, therefore, the gravel is by no means a homogeneous and continuous substance.

In the same way, a theory that some particular substance, say water, is homogeneous and continuous may be a good working theory up to a certain point, but may fail when we come to deal with quantities so minute or so attenuated that their heterogeneity of structure comes into prominence. Whether this heterogeneity of structure is or is not consistent with homogeneity and continuity of substance is another question.

The extreme form of the doctrine of continuity is that stated by Descartes, who maintains that the whole universe is equally full of matter, and that this matter is all of one kind, having no essential property besides that of extension. All the properties which we perceive in matter he reduces to its parts being movable among one another, and so capable of all the varieties which we can perceive to follow from the motion of its parts (*Principia*, ii. 23). Descartes's own attempts to deduce the different qualities and actions of bodies in this way are not of much value. More than a century was required to invent methods of investigating the conditions of the motion of systems of bodies such as Descartes imagined. But the hydrodynamical discovery of Helmholtz that a vortex in a perfect liquid possesses certain permanent characteristics, has been applied by Sir W. Thomson to form a theory of vortex atoms in a homogeneous, incompressible, and frictionless liquid, to which we shall return at the proper time.

OUTLINE OF MODERN MOLECULAR SCIENCE, AND IN PARTICULAR OF THE MOLECULAR THEORY OF GASES.

We begin by assuming that bodies are made up of parts, each of which is capable of motion, and that these parts act on each other in a manner consistent with the principle of the conservation of energy. In making these assumptions, we are justified by the facts that bodies may be divided into smaller parts, and that all bodies with which we are acquainted are conservative systems, which would not be the case unless their parts were also conservative systems.

We may also assume that these small parts are in motion. This is the most general assumption we can make, for it includes, as a particular case, the theory that the small parts are at rest. The phenomena of the diffusion of gases and liquids through each other show that there may be a motion of the small parts of a body which is not perceptible to us.

We make no assumption with respect to the nature of the small parts—whether they are all of one magnitude. We do not even assume them to have extension and figure. Each of them must be measured by its mass, and any two of them must, like visible bodies, have the power of acting on one another when they come near enough to do so. The properties of the body, or medium, are determined by the configuration and motion of its small parts.

The first step in the investigation is to determine the amount of motion which exists among the small parts, independent of the visible motion of the medium as a whole. For this purpose it is convenient to make use of a general theorem in dynamics due to Clausius.

When the motion of a material system is such that the time-average of the quantity $\Sigma(mx^2)$ remains constant, the state of the system is said to be that of stationary motion. When the motion of a material system is such that the sum of the moments of inertia of the system, about three axes at right angles through its centre of mass, never varies by more than small quantities from a constant value, the system is said to be in a state of stationary motion.

The kinetic energy of a particle is half the product of its mass into the square of its velocity, and the kinetic energy of a system is the sum of the kinetic energy of all its parts.

When an attraction or repulsion exists between two points, half the product of this stress into the distance between the two points is called the *virial* of the stress, and is reckoned positive when the stress is an attraction, and negative when it is a repulsion. The virial of a system is the sum of the virials of the stresses which exist in it. If the system is subjected to the external stress of the pressure of the sides of a vessel in which it is contained, this stress will introduce an amount of virial $\frac{2}{3}pV$, where p is the pressure on unit of area and V is the volume of the vessel.

The theorem of Clausius may now be stated as follows:—In a material system in a state of stationary motion the time-average of the kinetic energy is equal to the time-average of the virial. In the case of a fluid enclosed in a vessel

$$\frac{1}{2}\Sigma(m\bar{v}^2) = \frac{2}{3}pV + \frac{1}{2}\Sigma\Sigma(Rr),$$

where the first term denotes the kinetic energy, and is half the sum of the product of each mass into the mean square of its velocity. In the second term, p is the pressure on unit of surface of the vessel, whose volume is V , and the third term expresses the virial due to the internal actions between the parts of the system. A double symbol of summation is used, because every pair of parts between which any action exists must be taken into account. We have next to show that in gases the principal part of the pressure arises from the motion of the small parts of the medium, and not from a repulsion between them.

In the first place, if the pressure of a gas arises from the repulsion of its parts, the law of repulsion must be inversely as the distance. For, consider a cube filled with the gas at pressure p , and let the cube expand till each side is n times its former length. The pressure on unit of surface according to Boyle's law is now $\frac{p}{n^3}$, and since the area of a face of the cube is n^2 times what it was, the whole pressure on the face of the cube is $\frac{1}{n}$ of its original value.

But since everything has been expanded symmetrically, the distance between corresponding parts of the air is now n times what it was, and the force is n times less than it was. Hence the force must vary inversely as the distance.

But Newton has shown (*Principia*, bk. i. prop. 93) that this law is inadmissible, as it makes the effect of the distant parts of the medium on a particle greater than that of the neighbouring parts. Indeed, we should arrive at the conclusion that the pressure depends not only on the density of the air but on the form and dimensions of the vessel which contains it, which we know not to be the case.

If, on the other hand, we suppose the pressure to arise entirely from the motion of the molecules of the gas, the interpretation of Boyle's law becomes very simple. For, in this case

$$pV = \frac{1}{3}\Sigma(m\bar{v}^2).$$

The first term is the product of the pressure and the volume, which according to Boyle's law is constant for the same quantity of gas at the same temperature. The second term is two-thirds of the kinetic energy of the system, and we have every reason to believe that in gases when the temperature is constant the kinetic energy of unit of mass is also constant. If we admit that the kinetic energy of unit of mass is in a given gas proportional to the absolute temperature, this equation is the expression of the law of Charles as well as of that of Boyle, and may be written—

$$pV = R\theta,$$

where θ is the temperature reckoned from absolute zero, and R is a constant. The fact that this equation expresses with considerable accuracy the relation between the volume, pressure, and temperature of a gas when in an extremely rarified state, and that as the gas is more and more compressed the deviation from this equation becomes more apparent, shows that the pressure of a gas is due almost entirely to the motion of its molecules when the gas is rare, and that it is only when the density of the gas is considerably increased that the effect of direct action between the molecules becomes apparent.

The effect of the direct action of the molecules on each other depends on the number of pairs of molecules which at a given instant are near enough to act on one another. The number of such pairs is proportional to the square of the number of molecules in unit of volume, that is, to the square of the density of the gas. Hence, as long as the medium is so rare that the encounter between two molecules is not affected by the presence of others, the deviation from Boyle's law will be proportional to the square of the density. If the action between the molecules is on the whole repulsive, the pressure will be greater than that given by Boyle's law. If it is, on the whole, attractive, the pressure will be less than that given by Boyle's law. It appears, by the experiments of Regnault and others, that the pressure does deviate from Boyle's law when the density of the gas is increased. In the case of carbonic acid and other gases which are easily liquefied, this deviation is very great. In all cases, however, except that of hydrogen, the pressure is less than that given by Boyle's law, showing that the virial is on the whole due to attractive forces between the molecules.

Another kind of evidence as to the nature of the action between the molecules is furnished by an experiment made by Dr Joule. Of two vessels, one was exhausted and the other filled with a gas at a pressure of 20 atmospheres; and both were placed side by side in a vessel of water, which was constantly stirred. The temperature of the whole was observed. Then a communication was opened between the vessels, the compressed gas expanded to twice its volume, and the work of expansion, which at first produced a strong current in the gas, was soon converted into heat by the internal friction of the gas. When all was again at rest, and the temperature uniform, the temperature was again observed. In Dr Joule's original experiments the observed temperature was the same as before. In a series of experiments, conducted by Dr Joule and Sir W. Thomson on a different plan, by which the thermal effect of free expansion can be more accurately measured, a slight cooling effect was observed in all the gases examined except hydrogen. Since the temperature depends on the velocity of agitation of the molecules, it appears that when a gas expands without doing external work the velocity of agitation is not much affected, but that in most cases it is slightly diminished. Now, if the molecules during their mutual separation act on each other, their velocity will increase or diminish according as the force is repulsive or attractive. It appears, therefore, from the experiments on the free expansion of gases, that the force between the molecules is small but, on the whole, attractive.

Having thus justified the hypothesis that a gas consists of molecules in motion, which act on each other only when they come very close together during an encounter, but which, during the intervals between their encounters which constitute the greater part of their existence, are describing free paths, and are not acted on by any molecular force, we proceed to investigate the motion of such a system.

The mathematical investigation of the properties of such

a system of molecules in motion is the foundation of molecular science. Clausius was the first to express the relation between the density of the gas, the length of the free paths of its molecules, and the distance at which they encounter each other. He assumed, however, at least in his earlier investigations, that the velocities of all the molecules are equal. The mode in which the velocities are distributed was first investigated by the present writer, who showed that in the moving system the velocities of the molecules range from zero to infinity, but that the number of molecules whose velocities lie within given limits can be expressed by a formula identical with that which expresses in the theory of errors the number of errors of observation lying within corresponding limits. The proof of this theorem has been carefully investigated by Boltzmann,¹ who has strengthened it where it appeared weak, and to whom the method of taking into account the action of external forces is entirely due.

The mean kinetic energy of a molecule, however, has a definite value, which is easily expressed in terms of the quantities which enter into the expression for the distribution of velocities. The most important result of this investigation is that when several kinds of molecules are in motion and acting on one another, the mean kinetic energy of a molecule is the same whatever be its mass, the molecules of greater mass having smaller mean velocities. Now, when gases are mixed their temperatures become equal. Hence we conclude that the physical condition which determines that the temperature of two gases shall be the same is that the mean kinetic energies of agitation of the individual molecules of the two gases are equal. This result is of great importance in the theory of heat, though we are not yet able to establish any similar result for bodies in the liquid or solid state.

In the next place, we know that in the case in which the whole pressure of the medium is due to the motion of its molecules, the pressure on unit of area is numerically equal to two-thirds of the kinetic energy in unit of volume. Hence, if equal volumes of two gases are at equal pressures the kinetic energy is the same in each. If they are also at equal temperatures the mean kinetic energy of each molecule is the same in each. If, therefore, equal volumes of two gases are at equal temperatures and pressures, the number of molecules in each is the same, and therefore, the masses of the two kinds of molecules are in the same ratio as the densities of the gases to which they belong.

This statement has been believed by chemists since the time of Gay-Lussac, who first established that the weights of the chemical equivalents of different substances are proportional to the densities of these substances when in the form of gas. The definition of the word molecule, however, as employed in the statement of Gay-Lussac's law is by no means identical with the definition of the same word as in the kinetic theory of gases. The chemists ascertain by experiment the ratios of the masses of the different substances in a compound. From these they deduce the chemical equivalents of the different substances, that of a particular substance, say hydrogen, being taken as unity. The only evidence made use of is that furnished by chemical combinations. It is also assumed, in order to account for the facts of combination, that the reason why substances combine in definite ratios is that the molecules of the substances are in the ratio of their chemical equivalents, and that what we call combination is an action which takes place by a union of a molecule of one substance to a molecule of the other.

This kind of reasoning, when presented in a proper form and sustained by proper evidence, has a high degree of

cogency. But it is purely chemical reasoning; it is not dynamical reasoning. It is founded on chemical experience, not on the laws of motion.

Our definition of a molecule is purely dynamical. A molecule is that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas. The result of the kinetic theory, therefore, is to give us information about the relative masses of molecules considered as moving bodies. The consistency of this information with the deductions of chemists from the phenomena of combination, greatly strengthens the evidence in favour of the actual existence and motion of gaseous molecules.

Another confirmation of the theory of molecules is derived from the experiments of Dulong and Petit on the specific heat of gases, from which they deduced the law which bears their name, and which asserts that the specific heats of equal weights of gases are inversely as their combining weights, or, in other words, that the capacities for heat of the chemical equivalents of different gases are equal. We have seen that the temperature is determined by the kinetic energy of agitation of each molecule. The molecule has also a certain amount of energy of internal motion, whether of rotation or of vibration, but the hypothesis of Clausius, that the mean value of the internal energy always bears a proportion fixed for each gas to the energy of agitation, seems highly probable and consistent with experiment. The whole kinetic energy is therefore equal to the energy of agitation multiplied by a certain factor. Thus the energy communicated to a gas by heating it is divided in a certain proportion between the energy of agitation and that of the internal motion of each molecule. For a given rise of temperature the energy of agitation, say of a million molecules, is increased by the same amount whatever be the gas. The heat spent in raising the temperature is measured by the increase of the whole kinetic energy. The thermal capacities, therefore, of equal numbers of molecules of different gases are in the ratio of the factors by which the energy of agitation must be multiplied to obtain the whole energy. As this factor appears to be nearly the same for all gases of the same degree of atomicity, Dulong and Petit's law is true for such gases.

Another result of this investigation is of considerable importance in relation to certain theories,² which assume the existence of æthers or rare media consisting of molecules very much smaller than those of ordinary gases. According to our result, such a medium would be neither more nor less than a gas. Supposing its molecules so small that they can penetrate between the molecules of solid substances such as glass, a so-called vacuum would be full of this rare gas at the observed temperature, and at the pressure, whatever it may be, of the ætherial medium in space. The specific heat, therefore, of the medium in the so-called vacuum will be equal to that of the same volume of any other gas at the same temperature and pressure. Now, the purpose for which this molecular æther is assumed in these theories is to act on bodies by its pressure, and for this purpose the pressure is generally assumed to be very great. Hence, according to these theories, we should find the specific heat of a so-called vacuum very considerable compared with that of a quantity of air filling the same space.

We have now made a certain definite amount of progress towards a complete molecular theory of gases. We know the mean velocity of the molecules of each gas in metres per second, and we know the relative masses of the molecules of different gases. We also know that the molecules of one and the same gas are all equal in mass. For if they

¹ *Sitzungsberichte der K. K. Akad., Wien*, 8th Oct. 1868.

² See Gustav Hansemann, *Die Atome und ihre Bewegungen*. 1871. (H. G. Mayer.)

are not, the method of dialysis, as employed by Graham, would enable us to separate the molecules of smaller mass from those of greater, as they would stream through porous substances with greater velocity. We should thus be able to separate a gas, say hydrogen, into two portions, having different densities and other physical properties, different combining weights, and probably different chemical properties of other kinds. As no chemist has yet obtained specimens of hydrogen differing in this way from other specimens, we conclude that all the molecules of hydrogen are of sensibly the same mass, and not merely that their mean mass is a statistical constant of great stability.

But as yet we have not considered the phenomena which enable us to form an estimate of the actual mass and dimensions of a molecule. It is to Clausius that we owe the first definite conception of the free path of a molecule and of the mean distance travelled by a molecule between successive encounters. He showed that the number of encounters of a molecule in a given time is proportional to the velocity, to the number of molecules in unit of volume, and to the square of the distance between the centres of two molecules when they act on one another so as to have an encounter. From this it appears that if we call this distance of the centres the diameter of a molecule, and the volume of a sphere having this diameter the volume of a molecule, and the sum of the volumes of all the molecules the molecular volume of the gas, then the diameter of a molecule is a certain multiple of the quantity obtained by diminishing the free path in the ratio of the molecular volume of the gas to the whole volume of the gas. The numerical value of this multiple differs slightly, according to the hypothesis we assume about the law of distribution of velocities. It also depends on the definition of an encounter. When the molecules are regarded as elastic spheres we know what is meant by an encounter, but if they act on each other at a distance by attractive or repulsive forces of finite magnitude, the distance of their centres varies during an encounter, and is not a definite quantity. Nevertheless, the above statement of Clausius enables us, if we know the length of the mean path and the molecular volume of a gas, to form a tolerably near estimate of the diameter of the sphere of the intense action of a molecule, and thence of the number of molecules in unit of volume and the actual mass of each molecule. To complete the investigation we have, therefore, to determine the mean path and the molecular volume. The first numerical estimate of the mean path of a gaseous molecule was made by the present writer from data derived from the internal friction of air. There are three phenomena which depend on the length of the free path of the molecules of a gas. It is evident that the greater the free path the more rapidly will the molecules travel from one part of the medium to another, because their direction will not be so often altered by encounters with other molecules. If the molecules in different parts of the medium are of different kinds, their progress from one part of the medium to another can be easily traced by analysing portions of the medium taken from different places. The rate of diffusion thus found furnishes one method of estimating the length of the free path of a molecule. This kind of diffusion goes on not only between the molecules of different gases, but among the molecules of the same gas, only in the latter case the results of the diffusion cannot be traced by analysis. But the diffusing molecules carry with them in their free paths the momentum and the energy which they happen at a given instant to have. The diffusion of momentum tends to equalise the apparent motion of different parts of the medium, and constitutes the phenomenon called the internal friction or viscosity of gases. The diffusion of energy tends to equalise the

temperature of different parts of the medium, and constitutes the phenomenon of the conduction of heat in gases.

These three phenomena—the diffusion of matter, of motion, and of heat in gases—have been experimentally investigated,—the diffusion of matter by Graham and Loschmidt, the diffusion of motion by Oscar Meyer and Clerk Maxwell, and that of heat by Stefan.

These three kinds of experiments give results which in the present imperfect state of the theory and the extreme difficulty of the experiments, especially those on the conduction of heat, may be regarded as tolerably consistent with each other. At the pressure of our atmosphere, and at the temperature of melting ice, the mean path of a molecule of hydrogen is about the 10,000th of a millimetre, or about the fifth part of a wave-length of green light. The mean path of the molecules of other gases is shorter than that of hydrogen.

The determination of the molecular volume of a gas is subject as yet to considerable uncertainty. The most obvious method is that of compressing the gas till it assumes the liquid form. It seems probable, from the great resistance of liquids to compression, that their molecules are at about the same distance from each other as that at which two molecules of the same substance in the gaseous form act on each other during an encounter. If this is the case, the molecular volume of a gas is somewhat less than the volume of the liquid into which it would be condensed by pressure, or, in other words, the density of the molecules is somewhat greater than that of the liquid.

Now, we know the relative weights of different molecules with great accuracy, and, from a knowledge of the mean path, we can calculate their relative diameters approximately. From these we can deduce the relative densities of different kinds of molecules. The relative densities so calculated have been compared by Lorenz Meyer with the observed densities of the liquids into which the gases may be condensed, and he finds a remarkable correspondence between them. There is considerable doubt, however, as to the relation between the molecules of a liquid and those of its vapour, so that till a larger number of comparisons have been made, we must not place too much reliance on the calculated densities of molecules. Another, and perhaps a more refined, method is that adopted by M. Van der Waals, who deduces the molecular volume from the deviations of the pressure from Boyle's law as the gas is compressed.

The first numerical estimate of the diameter of a molecule was that made by Loschmidt in 1865 from the mean path and the molecular volume. Independently of him and of each other, Mr Stoney, in 1868, and Sir W. Thomson, in 1870, published results of a similar kind—those of Thomson being deduced not only in this way, but from considerations derived from the thickness of soap bubbles, and from the electric action between zinc and copper.

The diameter and the mass of a molecule, as estimated by these methods, are, of course, very small, but by no means infinitely so. About two millions of molecules of hydrogen in a row would occupy a millimetre, and about two hundred million million million of them would weigh a milligramme. These numbers must be considered as exceedingly rough guesses; they must be corrected by more extensive and accurate experiments as science advances; but the main result, which appears to be well established, is that the determination of the mass of a molecule is a legitimate object of scientific research, and that this mass is by no means immeasurably small.

Loschmidt illustrates these molecular measurements by a comparison with the smallest magnitudes visible by means of a microscope. Nobert, he tells us, can draw 4000 lines in the breadth of a millimetre. The intervals between

these lines can be observed with a good microscope. A cube, whose side is the 4000th of a millimetre, may be taken as the *minimum visibile* for observers of the present day. Such a cube would contain from 60 to 100 million molecules of oxygen or of nitrogen; but since the molecules of organised substances contain on an average about 50 of the more elementary atoms, we may assume that the smallest organised particle visible under the microscope contains about two million molecules of organic matter. At least half of every living organism consists of water, so that the smallest living being visible under the microscope does not contain more than about a million organic molecules. Some exceedingly simple organism may be supposed built up of not more than a million similar molecules. It is impossible, however, to conceive so small a number sufficient to form a being furnished with a whole system of specialised organs.

Thus molecular science sets us face to face with physiological theories. It forbids the physiologist from imagining that structural details of infinitely small dimensions can furnish an explanation of the infinite variety which exists in the properties and functions of the most minute organisms.

A microscopic germ is, we know, capable of development into a highly organised animal. Another germ, equally microscopic, becomes, when developed, an animal of a totally different kind. Do all the differences, infinite in number, which distinguish the one animal from the other, arise each from some difference in the structure of the respective germs? Even if we admit this as possible, we shall be called upon by the advocates of Pangenesis to admit still greater marvels. For the microscopic germ, according to this theory, is no mere individual, but a representative body, containing members collected from every rank of the long-drawn ramification of the ancestral tree, the number of these members being amply sufficient not only to furnish the hereditary characteristics of every organ of the body and every habit of the animal from birth to death, but also to afford a stock of latent gemmules to be passed on in an inactive state from germ to germ, till at last the ancestral peculiarity which it represents is revived in some remote descendant.

Some of the exponents of this theory of heredity have attempted to elude the difficulty of placing a whole world of wonders within a body so small and so devoid of visible structure as a germ, by using the phrase structureless germs.¹ Now, one material system can differ from another only in the configuration and motion which it has at a given instant. To explain differences of function and development of a germ without assuming differences of structure is, therefore, to admit that the properties of a germ are not those of a purely material system.

The evidence as to the nature and motion of molecules, with which we have hitherto been occupied, has been derived from experiments upon gaseous media, the smallest sensible portion of which contains millions of millions of molecules. The constancy and uniformity of the properties of the gaseous medium is the direct result of the inconceivable irregularity of the motion of agitation of its molecules. Any cause which could introduce regularity into the motion of agitation, and marshal the molecules into order and method in their evolutions, might check or even reverse that tendency to diffusion of matter, motion, and energy, which is one of the most invariable phenomena of nature, and to which Thomson has given the name of the dissipation of energy.

Thus, when a sound-wave is passing through a mass of

air, this motion is of a certain definite type, and if left to itself the whole motion is passed on to other masses of air, and the sound-wave passes on, leaving the air behind it at rest. Heat, on the other hand, never passes out of a hot body except to enter a colder body, so that the energy of sound-waves, or any other form of energy which is propagated so as to pass wholly out of one portion of the medium and into another, cannot be called heat.

We have now to turn our attention to a class of molecular motions, which are as remarkable for their regularity as the motion of agitation is for its irregularity.

It has been found, by means of the spectroscope, that the light emitted by incandescent substances is different according to their state of condensation. When they are in an extremely rarefied condition the spectrum of their light consists of a set of sharply-defined bright lines. As the substance approaches a denser condition the spectrum tends to become continuous, either by the lines becoming broader and less defined, or by new lines and bands appearing between them, till the spectrum at length loses all its characteristics and becomes identical with that of solid bodies when raised to the same temperature.

Hence the vibrating systems, which are the source of the emitted light, must be vibrating in a different manner in these two cases. When the spectrum consists of a number of bright lines, the motion of the system must be compounded of a corresponding number of types of harmonic vibration.

In order that a bright line may be sharply defined, the vibratory motion which produces it must be kept up in a perfectly regular manner for some hundreds or thousands of vibrations. If the motion of each of the vibrating bodies is kept up only during a small number of vibrations, then, however regular may be the vibrations of each body while it lasts, the resultant disturbance of the luminiferous medium, when analysed by the prism, will be found to contain, besides the part due to the regular vibrations, other motions, depending on the starting and stopping of each particular vibrating body, which will become manifest as a diffused luminosity scattered over the whole length of the spectrum. A spectrum of bright lines, therefore, indicates that the vibrating bodies when set in motion are allowed to vibrate in accordance with the conditions of their internal structure for some time before they are again interfered with by external forces.

It appears, therefore, from spectroscopic evidence that each molecule of a rarefied gas is, during the greater part of its existence, at such a distance from all other molecules that it executes its vibrations in an undisturbed and regular manner. This is the same conclusion to which we were led by considerations of another kind at p. 39.

We may therefore regard the bright lines in the spectrum of a gas as the result of the vibrations executed by the molecules while describing their free paths. When two molecules separate from one another after an encounter, each of them is in a state of vibration, arising from the unequal action on different parts of the same molecule during the encounter. Hence, though the centre of mass of the molecule describing its free path moves with uniform velocity, the parts of the molecule have a vibratory motion with respect to the centre of mass of the whole molecule, and it is the disturbance of the luminiferous medium communicated to it by the vibrating molecules which constitutes the emitted light.

We may compare the vibrating molecule to a bell. When struck, the bell is set in motion. This motion is compounded of harmonic vibrations of many different periods, each of which acts on the air, producing notes of as many different pitches. As the bell communicates its motion to the air, these vibrations necessarily decay, some

¹ See F. Galton, "On Blood Relationship," *Proc. Roy. Soc.*, June 13, 1872.

of them faster than others, so that the sound contains fewer and fewer notes, till at last it is reduced to the fundamental note of the bell.¹ If we suppose that there are a great many bells precisely similar to each other, and that they are struck, first one and then another, in a perfectly irregular manner, yet so that, on an average, as many bells are struck in one second of time as in another, and also in such a way that, on an average, any one bell is not again struck till it has ceased to vibrate, then the audible result will appear a continuous sound, composed of the sound emitted by bells in all states of vibration, from the clang of the actual stroke to the final hum of the dying fundamental tone.

But now let the number of bells be reduced while the same number of strokes are given in a second. Each bell will now be struck before it has ceased to vibrate, so that in the resulting sound there will be less of the fundamental tone and more of the original clang, till at last, when the peal is reduced to one bell, on which innumerable hammers are continually plying their strokes all out of time, the sound will become a mere noise, in which no musical note can be distinguished.

In the case of a gas we have an immense number of molecules, each of which is set in vibration when it encounters another molecule, and continues to vibrate as it describes its free path. The molecule is a material system, the parts of which are connected in some definite way, and from the fact that the bright lines of the emitted light have always the same wave-lengths, we learn that the vibrations corresponding to these lines are always executed in the same periodic time, and therefore the force tending to restore any part of the molecule to its position of equilibrium in the molecule must be proportional to its displacement relative to that position.

From the mathematical theory of the motion of such a system, it appears that the whole motion may be analysed into the following parts, which may be considered each independently of the others:—In the first place, the centre of mass of the system moves with uniform velocity in a straight line. This velocity may have any value. In the second place, there may be a motion of rotation, the angular momentum of the system about its centre of mass remaining during the free path constant in magnitude and direction. This angular momentum may have any value whatever, and its axis may have any direction. In the third place, the remainder of the motion is made up of a number of component motions, each of which is an harmonic vibration of a given type. In each type of vibration the periodic time of vibration is determined by the nature of the system, and is invariable for the same system. The relative amount of motion in different parts of the system is also determinate for each type, but the absolute amount of motion and the phase of the vibration of each type are determined by the particular circumstances of the last encounter, and may vary in any manner from one encounter to another.

The values of the periodic times of the different types of vibration are given by the roots of a certain equation, the form of which depends on the nature of the connections of the system. In certain exceptionally simple cases, as, for instance, in that of a uniform string stretched between two fixed points, the roots of the equation are connected by simple arithmetical relations, and if the internal structure of a molecule had an analogous kind of simplicity, we might expect to find in the spectrum of the molecule a

series of bright lines, whose wave-lengths are in simple arithmetical ratios.

But if we suppose the molecule to be constituted according to some different type, as, for instance, if it is an elastic sphere, or if it consists of a finite number of atoms kept in their places by attractive and repulsive forces, the roots of the equation will not be connected with each other by any simple relations, but each may be made to vary independently of the others by a suitable change of the connections of the system. Hence, we have no right to expect any definite numerical relations among the wave-lengths of the bright lines of a gas.

The bright lines of the spectrum of an incandescent gas are therefore due to the harmonic vibrations of the molecules of the gas during their free paths. The only effect of the motion of the centre of mass of the molecule is to alter the time of vibration of the light as received by a stationary observer. When the molecule is coming towards the observer, each successive impulse will have a shorter distance to travel before it reaches his eye, and therefore the impulses will appear to succeed each other more rapidly than if the molecule were at rest, and the contrary will be the case if the molecule is receding from the observer. The bright line corresponding to the vibration will therefore be shifted in the spectrum towards the blue end when the molecule is approaching, and towards the red end when it is receding from the observer. By observations of the displacement of certain lines in the spectrum, Dr Huggins and others have measured the rate of approach or of recession of certain stars with respect to the earth, and Mr Lockyer has determined the rate of motion of tornadoes in the sun. But Lord Rayleigh has pointed out that according to the dynamical theory of gases the molecules are moving hither and thither with so great velocity that, however narrow and sharply-defined any bright line due to a single molecule may be, the displacement of the line towards the blue by the approaching molecules, and towards the red by the receding molecules, will produce a certain amount of widening and blurring of the line in the spectrum, so that there is a limit to the sharpness of definition of the lines of a gas. The widening of the lines due to this cause will be in proportion to the velocity of agitation of the molecules. It will be greatest for the molecules of smallest mass, as those of hydrogen, and it will increase with the temperature. Hence the measurement of the breadth of the hydrogen lines, such as C or F in the spectrum of the solar prominences, may furnish evidence that the temperature of the sun cannot exceed a certain value.

ON THE THEORY OF VORTEX ATOMS.

The equations which form the foundations of the mathematical theory of fluid motion were fully laid down by Lagrange and the great mathematicians of the end of last century, but the number of solutions of cases of fluid motion which had been actually worked out remained very small, and almost all of these belonged to a particular type of fluid motion, which has been since named the irrotational type. It had been shown, indeed, by Lagrange, that a perfect fluid, if its motion is at any time irrotational, will continue in all time coming to move in an irrotational manner, so that, by assuming that the fluid was at one time at rest, the calculation of its subsequent motion may be very much simplified.

It was reserved for Helmholtz to point out the very remarkable properties of rotational motion in a homogeneous incompressible fluid devoid of all viscosity. We must first define the physical properties of such a fluid. In the first place, it is a material substance. Its motion is

¹ Part of the energy of motion is, in the case of the bell, dissipated in the substance of the bell in virtue of the viscosity of the metal, and assumes the form of heat, but it is not necessary, for the purpose of illustration, to take this cause of the decay of vibrations into account.

continuous in space and time, and if we follow any portion of it as it moves, the mass of that portion remains invariable. These properties it shares with all material substances. In the next place, it is incompressible. The form of a given portion of the fluid may change, but its volume remains invariable; in other words, the density of the fluid remains the same during its motion. Besides this, the fluid is homogeneous, or the density of all parts of the fluid is the same. It is also continuous, so that the mass of the fluid contained within any closed surface is always *exactly* proportional to the volume contained within that surface. This is equivalent to asserting that the fluid is not made up of molecules; for, if it were, the mass would vary in a discontinuous manner as the volume increases continuously, because first one and then another molecule would be included within the closed surface. Lastly, it is a perfect fluid, or, in other words, the stress between one portion and a contiguous portion is always normal to the surface which separates these portions, and this whether the fluid is at rest or in motion.

We have seen that in a molecular fluid the interdiffusion of the molecules causes an interdiffusion of motion of different parts of the fluid, so that the action between contiguous parts is no longer normal but in a direction tending to diminish their relative motion. Hence the perfect fluid cannot be molecular.

All that is necessary in order to form a correct mathematical theory of a material system is that its properties shall be clearly defined and shall be consistent with each other. This is essential; but whether a substance having such properties actually exists is a question which comes to be considered only when we propose to make some practical application of the results of the mathematical theory. The properties of our perfect liquid are clearly defined and consistent with each other, and from the mathematical theory we can deduce remarkable results, some of which may be illustrated in a rough way by means of fluids which are by no means perfect in the sense of not being viscous, such, for instance, as air and water.

The motion of a fluid is said to be irrotational when it is such that if a spherical portion of the fluid were suddenly solidified, the solid sphere so formed would not be rotating about any axis. When the motion of the fluid is rotational the axis and angular velocity of the rotation of any small part of the fluid are those of a *small* spherical portion suddenly solidified.

The mathematical expression of these definitions is as follows:—Let u, v, w be the components of the velocity of the fluid at the point (x, y, z) , and let

$$\alpha = \frac{dv}{dx} - \frac{dw}{dy}, \quad \beta = \frac{dw}{dx} - \frac{du}{dz}, \quad \gamma = \frac{du}{dy} - \frac{dv}{dx} \quad (1),$$

then α, β, γ are the components of the velocity of rotation of the fluid at the point (x, y, z) . The axis of rotation is in the direction of the resultant of α, β , and γ , and the velocity of rotation, ω , is measured by this resultant.

A line drawn in the fluid, so that at every point of the line

$$\frac{1}{\alpha} \frac{dx}{ds} = \frac{1}{\beta} \frac{dy}{ds} = \frac{1}{\gamma} \frac{dz}{ds} = \frac{1}{\omega} \quad (2),$$

where s is the length of the line from to the point x, y, z , is called a vortex line. Its direction coincides at every point with that of the axis of rotation of the fluid.

We may now prove the theorem of Helmholtz, that the points of the fluid which at any instant lie in the same vortex line continue to lie in the same vortex line during the whole motion of the fluid.

The equations of motion of a fluid are of the form

$$\rho \frac{du}{dt} + \frac{dp}{dx} + \rho \frac{dV}{dx} = 0 \quad (3),$$

when ρ is the density, which in the case of our homogeneous incompressible fluid we may assume to be unity, the operator $\frac{d}{dt}$ represents the rate of variation of the symbol to which it is prefixed at a point which is carried forward with the fluid, so that

$$\frac{du}{dt} = \frac{du}{dt} + u \frac{du}{dx} + v \frac{du}{dy} + w \frac{du}{dz} \quad (4),$$

p is the pressure, and V is the potential of external forces. There are two other equations of similar form in y and z . Differentiating the equation in y with respect to z , and that in z with respect to y , and subtracting the second from the first, we find

$$\frac{d}{dz} \frac{dv}{dt} - \frac{d}{dy} \frac{dw}{dt} = 0 \quad (5).$$

Performing the differentiations and remembering equations (1) and also the condition of incompressibility,

$$\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} = 0 \quad (6),$$

we find

$$\frac{d\alpha}{dt} = \alpha \frac{du}{dx} + \beta \frac{du}{dy} + \gamma \frac{du}{dz} \quad (7).$$

Now, let us suppose a vortex line drawn in the fluid so as always to begin at the same particle of the fluid. The components of the velocity of this point are u, v, w . Let us find those of a point on the moving vortex line at a distance ds from this point where

$$ds = \omega d\sigma \quad (8).$$

The co-ordinates of this point are

$$x + \alpha d\sigma, \quad y + \beta d\sigma, \quad z + \gamma d\sigma \quad (9),$$

and the components of its velocity are

$$u + \frac{d\alpha}{dt} d\sigma, \quad v + \frac{d\beta}{dt} d\sigma, \quad w + \frac{d\gamma}{dt} d\sigma \quad (10).$$

Consider the first of these components. In virtue of equation (7) we may write it

$$u + \frac{du}{dx} \alpha d\sigma + \frac{du}{dy} \beta d\sigma + \frac{du}{dz} \gamma d\sigma \quad (11),$$

or

$$u + \frac{du}{dx} \frac{dx}{ds} d\sigma + \frac{du}{dy} \frac{dy}{ds} d\sigma + \frac{du}{dz} \frac{dz}{ds} d\sigma \quad (12),$$

or

$$u + \frac{du}{ds} d\sigma \quad (13).$$

But this represents the value of the component u of the velocity of the fluid itself at the same point, and the same thing may be proved of the other components.

Hence the velocity of the second point on the vortex line is identical with that of the fluid at that point. In other words, the vortex line swims along with the fluid, and is always formed of the same row of fluid particles. The vortex line is therefore no mere mathematical symbol, but has a physical existence continuous in time and space.

By differentiating equations (1) with respect to x, y , and z respectively, and adding the results, we obtain the equation—

$$\frac{d\alpha}{dx} + \frac{d\beta}{dy} + \frac{d\gamma}{dz} = 0 \quad (14).$$

This is an equation of the same form with (6), which expresses the condition of flow of a fluid of invariable density. Hence, if we imagine a fluid, quite independent of the original fluid, whose components of velocity are α, β, γ , this imaginary fluid will flow without altering its density.

Now, consider a closed curve in space, and let vortex

lines be drawn in both directions from every point of this curve. These vortex lines will form a tubular surface, which is called a vortex tube or a vortex filament. Since the imaginary fluid flows along the vortex lines without change of density, the quantity which in unit of time flows through any section of the same vortex tube must be the same. Hence, at any section of a vortex tube the product of the area of the section into the mean velocity of rotation is the same. This quantity is called the *strength* of the vortex tube.

A vortex tube cannot begin or end within the fluid; for, if it did, the imaginary fluid, whose velocity components are α, β, γ , would be generated from nothing at the beginning of the tube, and reduced to nothing at the end of it. Hence, if the tube has a beginning and an end, they must lie on the surface of the fluid mass. If the fluid is infinite the vortex tube must be infinite, or else it must return into itself.

We have thus arrived at the following remarkable theorems relating to a finite vortex tube in an infinite fluid:—(1.) It returns into itself, forming a closed ring. We may therefore describe it as a vortex *ring*. (2.) It always consists of the same portion of the fluid. Hence its volume is invariable. (3.) Its strength remains always the same. Hence the velocity of rotation at any section varies inversely as the area of that section, and that of any segment varies directly as the length of that segment. (4.) No part of the fluid which is not originally in a state of rotational motion can ever enter into that state, and no part of the fluid whose motion is rotational can ever cease to move rotationally. (5.) No vortex tube can ever pass through any other vortex tube, or through any of its own convolutions. Hence, if two vortex tubes are linked together, they can never be separated, and if a single vortex tube is knotted on itself, it can never become untied. (6.) The motion at any instant of every part of the fluid, including the vortex rings themselves, may be accurately represented by conceiving an electric current to occupy the place of each vortex ring, the strength of the current being proportional to that of the ring. The magnetic force at any point of space will then represent in direction and magnitude the velocity of the fluid at the corresponding point of the fluid.

These properties of vortex rings suggested to Sir William Thomson¹ the possibility of founding on them a new form of the atomic theory. The conditions which must be satisfied by an atom are—permanence in magnitude, capability of internal motion or vibration, and a sufficient amount of possible characteristics to account for the difference between atoms of different kinds.

The small hard body imagined by Lucretius, and adopted by Newton, was invented for the express purpose of accounting for the permanence of the properties of bodies. But it fails to account for the vibrations of a molecule as revealed by the spectroscope. We may indeed suppose the atom elastic, but this is to endow it with the very property for the explanation of which, as exhibited in aggregate bodies, the atomic constitution was originally assumed. The massive centres of force imagined by Boscovich may have more to recommend them to the mathematician, who has no scruple in supposing them to be invested with the power of attracting and repelling according to any law of the distance which it may please him to assign. Such centres of force are no doubt in their own nature indivisible, but then they are also, singly, incapable of vibration. To obtain vibrations we must imagine molecules consisting of many such centres, but, in so doing, the possibility of these centres being separated altogether is again introduced.

Besides, it is in questionable scientific taste, after using atoms so freely to get rid of forces acting at sensible distances, to make the whole function of the atoms an action at insensible distances.

On the other hand, the vortex ring of Helmholtz, imagined as the true form of the atom by Thomson, satisfies more of the conditions than any atom hitherto imagined. In the first place, it is quantitatively permanent, as regards its volume and its strength,—two independent quantities. It is also qualitatively permanent as regards its degree of implication, whether “knottedness” on itself or “linkedness” with other vortex rings. At the same time, it is capable of infinite changes of form, and may execute vibrations of different periods, as we know that molecules do. And the number of essentially different implications of vortex rings may be very great without supposing the degree of implication of any of them very high.

But the greatest recommendation of this theory, from a philosophical point of view, is that its success in explaining phenomena does not depend on the ingenuity with which its contrivers “save appearances,” by introducing first one hypothetical force and then another. When the vortex atom is once set in motion, all its properties are absolutely fixed and determined by the laws of motion of the primitive fluid, which are fully expressed in the fundamental equations. The disciple of Lucretius may cut and carve his solid atoms in the hope of getting them to combine into worlds; the follower of Boscovich may imagine new laws of force to meet the requirements of each new phenomenon; but he who dares to plant his feet in the path opened up by Helmholtz and Thomson has no such resources. His primitive fluid has no other properties than inertia, invariable density, and perfect mobility, and the method by which the motion of this fluid is to be traced is pure mathematical analysis. The difficulties of this method are enormous, but the glory of surmounting them would be unique.

There seems to be little doubt that an encounter between two vortex atoms would be in its general character similar to those which we have already described. Indeed, the encounter between two smoke rings in air gives a very lively illustration of the elasticity of vortex rings.

But one of the first, if not the very first desideratum in a complete theory of matter is to explain—first, mass, and second, gravitation. To explain mass may seem an absurd achievement. We generally suppose that it is of the essence of matter to be the receptacle of momentum and energy, and even Thomson, in his definition of his primitive fluid, attributes to it the possession of mass. But according to Thomson, though the primitive fluid is the only true matter, yet that which we call matter is not the primitive fluid itself, but a mode of motion of that primitive fluid. It is the mode of motion which constitutes the vortex rings, and which furnishes us with examples of that permanence and continuity of existence which we are accustomed to attribute to matter itself. The primitive fluid, the only true matter, entirely eludes our perceptions when it is not endued with the mode of motion which converts certain portions of it into vortex rings, and thus renders it molecular.

In Thomson's theory, therefore, the mass of bodies requires explanation. We have to explain the inertia of what is only a mode of motion, and inertia is a property of matter, not of modes of motion. It is true that a vortex ring at any given instant has a definite momentum and a definite energy, but to show that bodies built up of vortex rings would have such momentum and energy as we know them to have is, in the present state of the theory, a very difficult task.

It may seem hard to say of an infant theory that it is bound to explain gravitation. Since the time of Newton,

¹ “On Vortex Atoms,” *Proc. Roy. Soc. Edin.*, 18th February 1867.

the doctrine of gravitation has been admitted and expounded, till it has gradually acquired the character rather of an ultimate fact than of a fact to be explained.

It seems doubtful whether Lucretius considers gravitation to be an essential property of matter, as he seems to assert in the very remarkable lines—

“Nam si tantundem est in lanæ glomere, quantum
Corporis in plumbo est, tantundem pendere par est :
Corporis officium est quoniam premere omnia deorsum.”
—*De Rerum Natura*, i. 361.

If this is the true opinion of Lucretius, and if the downward flight of the atoms arises, in his view, from their own gravity, it seems very doubtful whether he attributed the weight of sensible bodies to the impact of the atoms. The latter opinion is that of Le Sage, of Geneva, propounded in his *Lucrèce Newtonien*, and in his *Traité de Physique Mécanique*, published, along with a second treatise of his own, by Pierre Prevost, of Geneva, in 1818.¹ The theory of Le Sage is that the gravitation of bodies towards each other is caused by the impact of streams of atoms flying in all directions through space. These atoms he calls ultramundane corpuscles, because he conceives them to come in all directions from regions far beyond that part of the system of the world which is in any way known to us. He supposes each of them to be so small that a collision with another ultramundane corpuscle is an event of very rare occurrence. It is by striking against the molecules of gross matter that they discharge their function of drawing bodies towards each other. A body placed by itself in free space and exposed to the impacts of these corpuscles would be bandied about by them in all directions, but because, on the whole, it receives as many blows on one side as on another, it cannot thereby acquire any sensible velocity. But if there are two bodies in space, each of them will screen the other from a certain proportion of the corpuscular bombardment, so that a smaller number of corpuscles will strike either body on that side which is next the other body, while the number of corpuscles which strike it in other directions remains the same.

Each body will therefore be urged towards the other by the effect of the excess of the impacts it receives on the side furthest from the other. If we take account of the impacts of those corpuscles only which come directly from infinite space, and leave out of consideration those which have already struck mundane bodies, it is easy to calculate the result on the two bodies, supposing their dimensions small compared with the distance between them.

The force of attraction would vary directly as the product of the areas of the sections of the bodies taken normal to the distance and inversely as the square of the distance between them.

Now, the attraction of gravitation varies as the product of the masses of the bodies between which it acts, and inversely as the square of the distance between them. If, then, we can imagine a constitution of bodies such that the effective areas of the bodies are proportional to their masses, we shall make the two laws coincide. Here, then, seems to be a path leading towards an explanation of the law of gravitation, which, if it can be shown to be in other respects consistent with facts, may turn out to be a royal road into the very arcana of science.

Le Sage himself shows that, in order to make the effective area of a body, in virtue of which it acts as a screen to the streams of ultramundane corpuscles, proportional to the mass of the body, whether the body be large or small, we must admit that the size of the solid atoms of the body is exceedingly small compared with the distances between

them, so that a very small proportion of the corpuscles are stopped even by the densest and largest bodies. We may picture to ourselves the streams of corpuscles coming in every direction, like light from a uniformly illuminated sky. We may imagine a material body to consist of a congeries of atoms at considerable distances from each other, and we may represent this by a swarm of insects flying in the air. To an observer at a distance this swarm will be visible as a slight darkening of the sky in a certain quarter. This darkening will represent the action of the material body in stopping the flight of the corpuscles. Now, if the proportion of light stopped by the swarm is very small, two such swarms will stop nearly the same amount of light, whether they are in a line with the eye or not, but if one of them stops an appreciable proportion of light, there will not be so much left to be stopped by the other, and the effect of two swarms in a line with the eye will be less than the sum of the two effects separately.

Now, we know that the effect of the attraction of the sun and earth on the moon is not appreciably different when the moon is eclipsed than on other occasions when full moon occurs without an eclipse. This shows that the number of the corpuscles which are stopped by bodies of the size and mass of the earth, and even the sun, is very small compared with the number which pass straight through the earth or the sun without striking a single molecule. To the streams of corpuscles the earth and the sun are mere systems of atoms scattered in space, which present far more openings than obstacles to their rectilinear flight.

Such is the ingenious doctrine of Le Sage, by which he endeavours to explain universal gravitation. Let us try to form some estimate of this continual bombardment of ultramundane corpuscles which is being kept up on all sides of us.

We have seen that the sun stops but a very small fraction of the corpuscles which enter it. The earth, being a smaller body, stops a still smaller proportion of them. The proportion of those which are stopped by a small body, say a 1 lb shot, must be smaller still in an enormous degree, because its thickness is exceedingly small compared with that of the earth.

Now, the weight of the ball, or its tendency towards the earth, is produced, according to this theory, by the excess of the impacts of the corpuscles which come from above over the impacts of those which come from below, and have passed through the earth. Either of these quantities is an exceedingly small fraction of the momentum of the whole number of corpuscles which pass through the ball in a second, and their difference is a small fraction of either, and yet it is equivalent to the weight of a pound. The velocity of the corpuscles must be enormously greater than that of any of the heavenly bodies, otherwise, as may easily be shown, they would act as a resisting medium opposing the motion of the planets. Now, the energy of a moving system is half the product of its momentum into its velocity. Hence the energy of the corpuscles, which by their impacts on the ball during one second urge it towards the earth, must be a number of foot-pounds equal to the number of feet over which a corpuscle travels in a second, that is to say, not less than thousands of millions. But this is only a small fraction of the energy of all the impacts which the atoms of the ball receive from the innumerable streams of corpuscles which fall upon it in all directions.

Hence the rate at which the energy of the corpuscles is spent in order to maintain the gravitating property of a single pound, is at least millions of millions of foot-pounds per second.

What becomes of this enormous quantity of energy? If the corpuscles, after striking the atoms, fly off with a

¹ See also *Constitution de la Matière*, &c., par le P. Leray, Paris, 1863.

velocity equal to that which they had before, they will carry their energy away with them into the ultramundane regions. But if this be the case, then the corpuscles rebounding from the body in any given direction will be both in number and in velocity exactly equivalent to those which are prevented from proceeding in that direction by being deflected by the body, and it may be shown that this will be the case whatever be the shape of the body, and however many bodies may be present in the field. Thus, the rebounding corpuscles exactly make up for those which are deflected by the body, and there will be no excess of the impacts on any other body in one direction or another.

The explanation of gravitation, therefore, falls to the ground if the corpuscles are like perfectly elastic spheres, and rebound with a velocity of separation equal to that of approach. If, on the other hand, they rebound with a smaller velocity, the effect of attraction between the bodies will no doubt be produced, but then we have to find what becomes of the energy which the molecules have brought with them but have not carried away.

If any appreciable fraction of this energy is communicated to the body in the form of heat, the amount of heat so generated would in a few seconds raise it, and in like manner the whole material universe, to a white heat.

It has been suggested by Sir W. Thomson that the corpuscles may be so constructed so to carry off their energy with them, provided that part of their kinetic energy is transformed, during impact, from energy of translation to energy of rotation or vibration. For this purpose the corpuscles must be material systems, not mere points. Thomson suggests that they are vortex atoms, which are set into a state of vibration at impact, and go off with a smaller velocity of translation, but in a state of violent vibration. He has also suggested the possibility of the vortex corpuscle regaining its swiftness and losing part of its vibratory agitation by communion with its kindred corpuscles in infinite space.

We have devoted more space to this theory than it seems to deserve, because it is ingenious, and because it is the only theory of the cause of gravitation which has been so far developed as to be capable of being attacked and defended. It does not appear to us that it can account for the temperature of bodies remaining moderate while their atoms are exposed to the bombardment. The temperature of bodies must tend to approach that at which the average kinetic energy of a molecule of the body would be equal to the average kinetic energy of an ultramundane corpuscle.

Now, suppose a plane surface to exist which stops *all* the corpuscles. The pressure on this plane will be $p = NMu^2$ where M is the mass of a corpuscle, N the number in unit of volume, and u its velocity normal to the plane. Now, we know that the very greatest pressure existing in the universe must be much less than the pressure p , which would be exerted against a body which stops all the corpuscles. We are also tolerably certain that N , the number of corpuscles which are at any one time within unit of volume, is small compared with the value of N for the molecules of ordinary bodies. Hence, Mu^2 must be enormous compared with the corresponding quantity for ordinary bodies, and it follows that the impact of the corpuscles would raise all bodies to an enormous temperature. We may also observe that according to this theory the habitable universe, which we are accustomed to regard as the scene of a magnificent illustration of the conservation of energy as the fundamental principle of all nature, is in reality maintained in working order only by an enormous expenditure of external power, which would be nothing less than ruinous if the supply were drawn from anywhere else than from the infinitude of space, and which, if the contrivances of the most eminent mathematicians should be

found in any respect defective, might at any moment tear the whole universe atom from atom.

We must now leave these speculations about the nature of molecules and the cause of gravitation, and contemplate the material universe as made up of molecules. Every molecule, so far as we know, belongs to one of a definite number of species. The list of chemical elements may be taken as representing the known species which have been examined in the laboratories. Several of these have been discovered by means of the spectroscope, and more may yet remain to be discovered in the same way. The spectroscope has also been applied to analyse the light of the sun, the brighter stars, and some of the nebulae and comets, and has shown that the character of the light emitted by these bodies is similar in some cases to that emitted by terrestrial molecules, and in others to light from which the molecules have absorbed certain rays. In this way a considerable number of coincidences have been traced between the systems of lines belonging to particular terrestrial substances and corresponding lines in the spectra of the heavenly bodies.

The value of the evidence furnished by such coincidences may be estimated by considering the degree of accuracy with which one such coincidence may be observed. The interval between the two lines which form Fraunhofer's line D is about the five hundredth part of the interval between B and G on Kirchhoff's scale. A discordance between the positions of two lines amounting to the tenth part of this interval, that is to say, the five thousandth part of the length of the bright part of the spectrum, would be very perceptible in a spectroscope of moderate power. We may define the power of the spectroscope to be the number of times which the smallest measurable interval is contained in the length of the visible spectrum. Let us denote this by p . In the case we have supposed p will be about 5000.

If the spectrum of the sun contains n lines of a certain degree of intensity, the probability that any one line of the spectrum of a gas will coincide with one of these n lines is

$$1 - \left(1 - \frac{1}{p}\right)^n = \frac{n}{p} \left(1 - \frac{n-1}{2} \frac{1}{p} + \&c.\right),$$

and when p is large compared with n , this becomes nearly $\frac{n}{p}$. If there are r lines in the spectrum of the gas, the probability that each and every one shall coincide with a line in the solar spectrum is approximately $\frac{nr}{p^r}$.

Hence, in the case of a gas whose spectrum contains several lines, we have to compare the results of two hypotheses. If a large amount of the gas exists in the sun, we have the strongest reason for expecting to find all the r lines in the solar spectrum. If it does not exist, the probability that r lines out of the n observed lines shall coincide with the lines of the gas is exceedingly small. If, then, we find all the r lines in their proper places in the solar spectrum, we have very strong grounds for believing that the gas exists in the sun. The probability that the gas exists in the sun is greatly strengthened if the character of the lines as to relative intensity and breadth is found to correspond in the two spectra.

The absence of one or more lines of the gas in the solar spectrum tends of course to weaken the probability, but the amount to be deducted from the probability must depend on what we know of the variation in the relative intensity of the lines when the temperature and the pressure of the gas are made to vary.

Coincidences observed, in the case of several terrestrial substances, with several systems of lines in the spectra of the heavenly bodies, tend to increase the evidence for the

doctrine that terrestrial substances exist in the heavenly bodies, while the discovery of particular lines in a celestial spectrum which do not coincide with any line in a terrestrial spectrum does not much weaken the general argument, but rather indicates either that a substance exists in the heavenly body not yet detected by chemists on earth, or that the temperature of the heavenly body is such that some substance, undecomposable by our methods, is there split up into components unknown to us in their separate state.

We are thus led to believe that in widely-separated parts of the visible universe molecules exist of various kinds, the molecules of each kind having their various periods of vibration either identical, or so nearly identical that our spectroscopes cannot distinguish them. We might argue from this that these molecules are alike in all other respects, as, for instance, in mass. But it is sufficient for our present purpose to observe that the same kind of molecule, say that of hydrogen, has the same set of periods of vibration, whether we procure the hydrogen from water, from coal, or from meteoric iron, and that light, having the same set of periods of vibration, comes to us from the sun, from Sirius, and from Arcturus.

The same kind of reasoning which led us to believe that hydrogen exists in the sun and stars, also leads us to believe that the molecules of hydrogen in all these bodies had a common origin. For a material system capable of vibration may have for its periods of vibration any set of values whatever. The probability, therefore, that two material systems, quite independent of each other, shall have, to the degree of accuracy of modern spectroscopic measurements, the same set of periods of vibration, is so very small that we are forced to believe that the two systems are not independent of each other. When, instead of two such systems, we have innumerable multitudes all having the same set of periods, the argument is immensely strengthened.

Admitting, then, that there is a real relation between any two molecules of hydrogen, let us consider what this relation may be.

We may conceive of a mutual action between one body and another tending to assimilate them. Two clocks, for instance, will keep time with each other if connected by a wooden rod, though they have different rates if they were disconnected. But even if the properties of a molecule were as capable of modification as those of a clock, there is no physical connection of a sufficient kind between Sirius and Arcturus.

There are also methods by which a large number of bodies differing from each other may be sorted into sets, so that those in each set more or less resemble each other. In the manufacture of small shot this is done by making the shot roll down an inclined plane. The largest specimens acquire the greatest velocities, and are projected farther than the smaller ones. In this way the various pellets, which differ both in size and in roundness, are sorted into different kinds, those belonging to each kind being nearly of the same size, and those which are not tolerably spherical being rejected altogether.

If the molecules were originally as various as these leaden pellets, and were afterwards sorted into kinds, we should have to account for the disappearance of all the molecules which did not fall under one of the very limited number of kinds known to us; and to get rid of a number of indestructible bodies, exceeding by far the number of the molecules of all the recognised kinds, would be one of the severest labours ever proposed to a cosmogonist.

It is well known that living beings may be grouped into a certain number of species, defined with more or less precision, and that it is difficult or impossible to find a series of individuals forming the links of a continuous chain between one species and another. In the case of living beings,

however, the generation of individuals is always going on, each individual differing more or less from its parents. Each individual during its whole life is undergoing modification, and it either survives and propagates its species, or dies early, accordingly as it is more or less adapted to the circumstances of its environment. Hence, it has been found possible to frame a theory of the distribution of organisms into species by means of generation, variation, and discriminative destruction. But a theory of evolution of this kind cannot be applied to the case of molecules, for the individual molecules neither are born nor die, they have neither parents nor offspring, and so far from being modified by their environment, we find that two molecules of the same kind, say of hydrogen, have the same properties, though one has been compounded with carbon and buried in the earth as coal for untold ages, while the other has been "occluded" in the iron of a meteorite, and after unknown wanderings in the heavens has at last fallen into the hands of some terrestrial chemist.

The process by which the molecules become distributed into distinct species is not one of which we know any instances going on at present, or of which we have as yet been able to form any mental representation. If we suppose that the molecules known to us are built up each of some moderate number of atoms, these atoms being all of them exactly alike, then we may attribute the limited number of molecular species to the limited number of ways in which the primitive atoms may be combined so as to form a permanent system.

But though this hypothesis gets rid of the difficulty of accounting for the independent origin of different species of molecules, it merely transfers the difficulty from the known molecules to the primitive atoms. How did the atoms come to be all alike in those properties which are in themselves capable of assuming any value?

If we adopt the theory of Boscovich, and assert that the primitive atom is a mere centre of force, having a certain definite mass, we may get over the difficulty about the equality of the mass of all atoms by laying it down as a doctrine which cannot be disproved by experiment, that mass is not a quantity capable of continuous increase or diminution, but that it is in its own nature discontinuous, like number, the atom being the unit, and all masses being multiples of that unit. We have no evidence that it is possible for the ratio of two masses to be an incommensurable quantity, for the incommensurable quantities in geometry are supposed to be traced out in a continuous medium. If matter is atomic, and therefore discontinuous, it is unfitted for the construction of perfect geometrical models, but in other respects it may fulfil its functions.

But even if we adopt a theory which makes the equality of the mass of different atoms a result depending on the nature of mass rather than on any quantitative adjustment, the correspondence of the periods of vibration of actual molecules is a fact of a different order.

We know that radiations exist having periods of vibration of every value between those corresponding to the limits of the visible spectrum, and probably far beyond these limits on both sides. The most powerful spectroscope can detect no gap or discontinuity in the spectrum of the light emitted by incandescent lime.

The period of vibration of a luminous particle is therefore a quantity which in itself is capable of assuming any one of a series of values, which, if not mathematically continuous, is such that consecutive observed values differ from each other by less than the ten thousandth part of either. There is, therefore, nothing in the nature of time itself to prevent the period of vibration of a molecule from assuming any one of many thousand different observable

values. That which determines the period of any particular kind of vibration is the relation which subsists between the corresponding type of displacement and the force of restitution thereby called into play, a relation involving constants of space and time as well as of mass.

It is the equality of these space- and time-constants for all molecules of the same kind which we have next to consider. We have seen that the very different circumstances in which different molecules of the same kind have been placed have not, even in the course of many ages, produced any appreciable difference in the values of these constants. If, then, the various processes of nature to which these molecules have been subjected since the world began have not been able in all that time to produce any appreciable difference between the constants of one molecule and those of another, we are forced to conclude that it is not to the operation of any of these processes that the uniformity of the constants is due.

The formation of the molecule is therefore an event not belonging to that order of nature under which we live. It is an operation of a kind which is not, so far as we are aware, going on on earth or in the sun or the stars, either now or since these bodies began to be formed. It must be referred to the epoch, not of the formation of the earth or of the solar system, but of the establishment of the existing order of nature, and till not only these worlds and systems, but the very order of nature itself is dissolved, we have no reason to expect the occurrence of any operation of a similar kind.

In the present state of science, therefore, we have strong reasons for believing that in a molecule, or if not in a molecule, in one of its component atoms, we have something which has existed either from eternity or at least from times anterior to the existing order of nature. But besides this atom, there are immense numbers of other atoms of the same kind, and the constants of each of these atoms are incapable of adjustment by any process now in action. Each is physically independent of all the others.

Whether or not the conception of a multitude of beings existing from all eternity is in itself self-contradictory, the conception becomes palpably absurd when we attribute a relation of quantitative equality to all these beings. We are then forced to look beyond them to some common cause or common origin to explain why this singular relation of equality exists, rather than any one of the infinite number of possible relations of inequality.

Science is incompetent to reason upon the creation of matter itself out of nothing. We have reached the utmost limit of our thinking faculties when we have admitted that, because matter cannot be eternal and self-existent, it must have been created. It is only when we contemplate not matter in itself, but the form in which it actually exists, that our mind finds something on which it can lay hold.

That matter, as such, should have certain fundamental properties, that it should have a continuous existence in space and time, that all action should be between two portions of matter, and so on, are truths which may, for aught we know, be of the kind which metaphysicians call necessary. We may use our knowledge of such truths for purposes of deduction, but we have no data for speculating on their origin.

But the equality of the constants of the molecules is a fact of a very different order. It arises from a particular distribution of matter, a *collocation*, to use the expression of Dr Chalmers, of things which we have no difficulty in imagining to have been arranged otherwise. But many of the ordinary instances of collocation are adjustments of constants, which are not only arbitrary in their own nature, but in which variations actually occur; and when it is pointed out that these adjustments are beneficial to living beings, and are therefore instances of benevolent design, it is replied that those variations which are not conducive to the growth and multiplication of living beings tend to their destruction, and to the removal thereby of the evidence of any adjustment not beneficial.

The constitution of an atom, however, is such as to render it, so far as we can judge, independent of all the dangers arising from the struggle for existence. Plausible reasons may, no doubt, be assigned for believing that if the constants had varied from atom to atom through any sensible range, the bodies formed by aggregates of such atoms would not have been so well fitted for the construction of the world as the bodies which actually exist. But as we have no experience of bodies formed of such variable atoms this must remain a bare conjecture.

Atoms have been compared by Sir J. Herschel to manufactured articles, on account of their uniformity. The uniformity of manufactured articles may be traced to very different motives on the part of the manufacturer. In certain cases it is found to be less expensive as regards trouble, as well as cost, to make a great many objects exactly alike than to adapt each to its special requirements. Thus, shoes for soldiers are made in large numbers without any designed adaptation to the feet of particular men. In another class of cases the uniformity is intentional, and is designed to make the manufactured article more valuable. Thus, Whitworth's bolts are made in a certain number of sizes, so that if one bolt is lost, another may be got at once, and accurately fitted to its place. The identity of the arrangement of the words in the different copies of a document or book is a matter of great practical importance, and it is more perfectly secured by the process of printing than by that of manuscript copying.

In a third class not a part only but the whole of the value of the object arises from its exact conformity to a given standard. Weights and measures belong to this class, and the existence of many well-adjusted material standards of weight and measure in any country furnishes evidence of the existence of a system of law regulating the transactions of the inhabitants, and enjoining in all professed measures a conformity to the national standard.

There are thus three kinds of usefulness in manufactured articles—cheapness, serviceableness, and quantitative accuracy. Which of these was present to the mind of Sir J. Herschel we cannot now positively affirm, but it was at least as likely to have been the last as the first, though it seems more probable that he meant to assert that a number of exactly similar things cannot be each of them eternal and self-existent, and must therefore have been made, and that he used the phrase "manufactured article" to suggest the idea of their being made in great numbers.

(J. C. M.)

Section V

THE ATOMIC DEBATES

William Odling was one of the outstanding English theoretical chemists of the day, who had been a delegate at the Karlsruhe Conference. By 1864 atomic weights were at last agreed upon; but isomerism still remained unexplained. Further, Sir John Herschel, an astronomer and philosopher of science, had complained that chemical symbols did not obey clearly defined rules like those of algebra. In his *Calculus*, Benjamin Brodie, the son of a physiologist President of the Royal Society of the same name, sought to remedy this, though he could never account for isomerism. Brodie was Professor of Chemistry at Oxford, and had introduced laboratory teaching there. He had himself been trained under Liebig; and had been influenced by the formal logic of George Boole. He is best known for his work on ozone.

Brodie's lecture set off debates which read like dramatic works by a philosopher of science. Maxwell tried to argue that the dynamical theory of gases provided evidence for the granular nature of matter; a point to which he returned on later occasions. But chemists were not yet ready to listen. Brodie's suggestion that many elements might be complex bodies aroused most attention. The debate was reported in William Crookes' *Chemical News*.

J. C. Brough's *Laboratory* was a journal which paid its contributors, and hence within a year it disappeared although it had attracted a number of interesting articles. Kekulé's paper was meant to be the first of a series, which was cut off by the journal's collapse. He argued, as did Alexander Williamson in 1869, for chemical atoms; for a minimal theory on which everybody could agree. Williamson had made his reputation with papers on the ethers, and was Professor at University College, London. He had been a pupil of the positivist philosopher Auguste Comte, but in these debates it was Brodie who took up the extreme positivistic position, and Williamson who defended the atomic theory. His lecture was apparently delivered from unarranged notes, and this accounts for its loose organisation. Williamson paid no attention to Brodie's *Calculus*, and attacked the upholders of equivalents, claiming that in fact they used the atomic theory even though they claimed not to.

His address was so long that there was no time for discussion, and at the next meeting of the Chemical Society Dumas was to deliver his Faraday Lecture (reprinted in Section III). So the debate on Williamson's speech was long delayed. And when it came, Brodie's tart introduction set off a spirited discussion, which apparently became more heated than the printed accounts imply. The odder contributions were those from Carey Foster, a physicist, and Edmund Mills, a physical chemist. Carey Foster argued that chemical combination might be akin to transmutation, a view not unlike that of Coleridge and Hegel; those in a Kantian tradition insisted through the century on the inadequacy of an atomic explanation of the properties of compounds, since these were so different from those of the component elements.

Mills's contribution would seem to have been the suggestion that atoms were not a reasonable basis for a scientific theory, whereas waves were, because the latter were a fact, or a *vera causa*. That is to say, we know about waves, for we can observe them, and we know what we are doing when we take waves as a model in the undulatory theory of light. With atoms, on the other hand, we are unfamiliar; we assign to them properties *ad hoc*; and such entities can never be other than fictions. The wave theory of light and the atomic theory are therefore not comparable. In his erudite paper in the *Philosophical Magazine* two years later, Mills expanded the points made in the debate. The atomic theory is crude guesswork, embodying the materialistic fallacy; even its success would not prove the existence of atoms, and anyway the laws of chemical combination do not demand atomic explanation. The best thinkers of the past had rejected it; and so should chemists, looking instead at motion, or energy.

FURTHER READING

W. H. Brock (ed.), *The Atomic Debates*, Leicester, 1967

CHEMISTRY.

Address by WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Secretary to the Chemical Society, Lecturer on Chemistry at St. Bartholomew's Hospital.

At the Leeds Meeting of the British Association in 1858, Sir John Herschel, the then President of the Chemical Section, opened its proceedings with an introductory address of singular interest, and thereby established a precedent which, with a solitary exception, has been uniformly adopted by successive occupants of the position which I have now the honour to hold. Following in his footsteps, *longo intervallo*, I in my turn now venture upon a few words of introduction to the proper business that we have in hand. In the first place, I may congratulate the Section upon the presence among us of so many distinguished chemists, including several of my more immediate predecessors. I need scarcely express the personal gratification I feel at meeting them here, nor say how much their presence relieves me from the feeling of responsibility and self-mistrust with which I undertook the honourable office so kindly entrusted to me by the General Committee, feeling now that, upon any occasion of difficulty, I shall have them to apply to for counsel and assistance.

After the great diversity, or rather antagonism, of opinion which has existed for the last dozen years or so, I am almost bound to take a somewhat prominent notice of the substantial agreement which now prevails among English chemists as to the combining proportions of the elementary bodies and the molecular weights of their most important compounds. The present unanimity of opinion on this fundamental subject among those who have given it their attention is, I conceive, greater than has ever been the case since Dalton published his 'New System of Chemical Philosophy,' more than half a century ago. As yet, indeed, the unanimity of practice falls considerably short of the unanimity of belief; but, even in this direction, great progress is being made, to which the publication of Miller's 'Elements of Chemistry,' Watts's 'Dictionary of Chemistry,' and Hofmann's 'Jury Report on the Chemical Products in the Great Exhibition,' will doubtless give a yet stronger impetus. As was well observed by Dr. Miller at a previous Meeting of this Association, "Chemistry is not merely a science; it is also an art, which has introduced its nomenclature and its notation into our manufactories, and in some measure even

into our daily life." Hence the great difficulty of effecting a speedy change in chemical usages alike so time-honoured and intimately ramified with the affairs of our everyday existence. I propose, by your permission, to make a few remarks upon the history of this chemical reformation, more especially in connexion with certain points which one or two of its acknowledged leaders have scarcely, I think, correctly estimated.

From the time when Dalton first introduced the expression "atomic weight," up to the year 1842, when Gerhardt announced his views upon the molecular constitution of water, there does not appear to have been any marked difference of opinion among chemists as to the combining proportions of the principal elements. That 1 part by weight of hydrogen united with 36 parts by weight of chlorine to form a single molecule of hydrochloric acid, and with 8 parts by weight of oxygen to form a single molecule of water, was the notion both of Berzelius and Gmelin, who may be taken as representatives of the two chief Continental schools of theoretic chemistry. Indeed, no doubts seem to have been entertained in their time as to the combining proportions of the three elements. Using the hydrogen scale of numbers, both chemists represented the combining proportion of hydrogen as 1, that of chlorine as 36, and that of oxygen as 8. Both, moreover, represented the molecular weight of hydrochloric acid as 37, and the molecular weight of water as 9. It is true that Berzelius professedly regarded the single combining proportions of hydrogen and chlorine as consisting each of two physical atoms; but, since the two atoms of hydrogen, for instance, which constituted the one combining proportion of hydrogen, were chemically inseparable from one another, they were really tantamount to one atom only of hydrogen, and, in point of fact, were always employed by Berzelius as representing the single chemical atom of hydrogen, or its smallest actual combining proportion. Distinguishing thus between the physical atom and the combining proportion, Berzelius's recognition of the truth, that equal volumes of the elementary gases contain an equal number of atoms, was utterly barren. But, identifying the physical atom with the combining proportion, Gerhardt's recognition, or rather establishment, of the broader truth, that equal volumes of all gases, elementary and compound, contain the same number of atoms, has been in the highest degree prolific. From Gerhardt's division of volatile bodies into a majority whose recognized molecules corresponded respectively with four volumes of vapour, and a minority whose recognized molecules corresponded respectively with but two volumes, and from his proposal, in conjunction with Laurent, to double the molecular weights of these last, so as to make the molecules of all volatile bodies, simple and compound, correspond each with four volumes of vapour, must, I conceive, be traced the development by himself and others of the matured views on chemical philosophy which now prevail. With every respect for my predecessor in this chair, and for the accomplished author of the '*Leçons de Philosophie Chimique*,' from neither of whom do I ever venture to differ without fear and trembling, I cannot join with them in regarding the initiation of Gerhardt's system as an imperfect return, and its remarkable maturation in these recent days as a more complete return to the notions of Berzelius. Although, indeed, the elementary weights now employed, with the exception of those for some half-dozen metals, are identical with the atomic weights of Berzelius, yet so unlike are they to his combining weights that fully four-fifths of all known compounds have to be expressed by formulæ entirely different from his—namely, all those bodies, with but very few exceptions, into which hydrogen, fluorine, chlorine, bromine, iodine, nitrogen, phosphorus, arsenic, boron, and the metals lithium, sodium, potassium, silver, and gold, enter as constituents. Fully admitting that the new system of atomic weights, as it now exists, is the joint product of many minds—fully admitting that it owes its present general acceptance chiefly to the introduction of the water type by Williamson during Gerhardt's lifetime, and the recognition of diatomic metals by Wurtz and Cannizzaro, after his decease—and fully admitting, moreover, that some of Gerhardt's steps in the development of his unitary system were decidedly, though perhaps excusably, retrograde, I yet look upon him, not I trust with the fond admiration of the pupil, but with the calm judgment of the chemist, as being the great founder of that modern chemical philosophy in the general spread of which I have already ventured to congratulate the Members of the Section.

Prior to the time of Gerhardt, the selection of molecular weights for different bodies, elementary and compound, had been almost a matter of hazard. Relying conjointly upon physical and chemical phenomena, he first established definite principles of selection, by pointing out the considerations upon which the determination of atomic weights must logically depend. Relying upon these principles, he established his classification of the non-metallic elements into monhydrides, represented by chlorine; dihydrides, represented by oxygen; trihydrides, represented by nitrogen, &c.; and, relying upon the same principles, but with a greatly increased knowledge of phenomena, later chemists have given to his method a development and unity, more especially as regards the metallic elements, which have secured for the new system the impregnable and acknowledged position which it at present occupies. The comparative unanimity which prevailed before the time of Gerhardt was the unanimity of submission to authority; but the greater unanimity which now prevails is the unanimity of conviction consequent upon an intermediate period of solitary insurrection, general disturbance, and ultimate triumph.

Bearing in mind how much the origin of the new system by Gerhardt, and its completion by his colleagues and disciples, are due to a correct appreciation of the harmony subsisting between chemical and physical relations, we cannot but give a hearty welcome to any large exposition of mixed chemico-physical phenomena; and, whether or not we agree with all his conclusions, there can be but one opinion as to the obligation chemists are under to Professor Kopp, of Giessen, for the great addition he has recently made to our knowledge and means of obtaining a further knowledge of what has hitherto been but a very limited subject—namely, specific heat.

The agreement of chemists as to the elemental atomic weights is tantamount to an agreement among them as to the relative quantities of the different kinds of matter which shall be represented by the different elemental symbols; and this brings me to the subject of chemical notation. At one time many chemists, even of considerable eminence, believed and taught that Gerhardt's reformation had reference mainly to notation, and not to the association and interpretation of phenomena, and it became rather a fashion among them to declaim against the puerilities of notational questions. That the idea is of far greater importance than the mode of expressing it, is an obvious truism; nevertheless the mode of expression has an importance of its own, as facilitating the spread of the idea, and more especially its development and procreation. It has been well asked, in what position would the science of arithmetic have been but for the substitution of Arabic for Roman numerals, the notation in which value is expressed by the change in position for that in which it is expressed mainly by the repetition of a few simple signs? It is unfortunately too true that chemical notation is at present in anything but a satisfactory state. The much-used sign of addition is, I conceive, about the last one would deliberately select to represent the fine idea of chemical combination, which seems allied rather, I should say, to an interpenetration than to a coarse apposition of atoms. The placing of symbols in contiguity, or simply introducing a point between them, as indicative of a sort of multiplication or involution of the one atom into the other, is, I think, far preferable; but here, as pointed out by Sir John Herschel, we violate the ordinary algebraic understanding, which assigns very different numerical values to the expressions XY and $X+Y$ respectively. I know, indeed, that one among us has been engaged for some years past in conceiving and working out a new and strictly philosophical system of chemical notation by means of actual formulæ, instead of mere symbols; and I am sure that I only express the general wish of the Section when I ask Sir Benjamin Brodie not to postpone the publication of his views for a longer time than is absolutely necessary for their sufficient elaboration. In any case, however, the symbolic notation at present employed, with more or less modification of detail, must continue to have its peculiar uses as an instrument of interpretation; and hence the importance of our endeavouring to render it more precise in meaning and consistent in its application. Many of its incongruities belong to the very lowest order of convention; such, for example, as the custom of distinguishing between the representation of so-called mineral and organic compounds, one particular sequence of symbols being habitually employed in repre-

senting the compounds of carbon, and an entirely different sequence of symbols in representing the more or less analogous compounds of all other elements. Now that organic and mineral chemistry are properly regarded as forming one continuous whole, a conclusion to which in my opinion Kolbe's researches on sulphuretted organic bodies have largely contributed, it is high time that such relics of the ancient superstition that organic and mineral chemistry were essentially different from one another should be done away with.

Although, during the past year, the direct advance of that crucial organic chemistry, the synthesis of natural organic bodies, has not been striking, yet, on the other hand, its indirect advance has, I submit, been very considerable. Several of the artificially produced organic compounds, at first thought to be identical with those of natural origin, have proved to be, as is well known, not identical, but only isomeric therewith. Hence, *reculer pour mieux sauter*, chemists have been stepping back a little to examine more intimately the constitution both of natural organic bodies and of their artificial isomers. The synthetic power having been attained of putting the bricks together in almost any desired way, it is yet necessary, in order to construct some particular biological edifice, first to learn the way in which its constituent bricks have been naturally put together. We accordingly find the study of isomerism, or, what comes to the same thing, the study of the intimate constitution of bodies, assuming an importance never before accorded to it. Isomerism is, in fact, the chemical problem of the day, and concurrently with its rapidly advancing solution, through the varied endeavours of many workers, will be the advance in rational organic synthesis. It is curious to note the oscillations of opinion in reference to this subject. Twenty years ago the molecular constitution of bodies was perceived by a special instinct, simultaneously with, or even prior to, the establishment of their molecular weights. Then came an interval of scepticism, when the intimate constitution of bodies was maintained to be not only unknown, but unknowable. Now we have a period of temperate reaction, not recognizing the desired knowledge as unattainable, but only as difficult of attainment. And in this, as in many other instances, we find evidence of the healthier state of mind in which, now more perhaps than ever, the first principles of chemical philosophy are explored. Speculation, indeed, is not less rife and scarcely less esteemed than formerly, but is now seldom or never mistaken for ascertained truth. Scepticism, indeed, still prevails—not, however, the sterile scepticism of resignation, but the fertile scepticism which aspires to greater and greater certainty of knowledge. Chemical science is advancing, I believe, not only more rapidly, but upon a surer basis than heretofore; and, while with every advance the prospect widens before our eyes, so that we become almost alarmed at contemplating what those who come after us will have to learn, we console ourselves with the determination that their labour of unlearning shall be as little as possible—far less, we hope, than what we in our time have had to experience.

CHEMICAL SOCIETY.

Thursday, June 6, 1867.

DR. A. W. WILLIAMSON, F.R.S., *Vice-President, in the Chair.*

The minutes of the previous meeting were read and confirmed.

SIR BENJAMIN C. BRODIE, Bart., Professor of Chemistry in the University of Oxford, then delivered the following lecture:—

"On the Mode of Representation afforded by the Chemical Calculus, as contrasted with the Atomic Theory."

MR. PRESIDENT,—I feel that I have undertaken this evening a truly difficult task, which is to give to the Chemical Society, in the brief space of one hour, an account of a somewhat abstruse and difficult subject, the exact comprehension of which requires that it should be minutely considered in all its details. I should not, however, shrink from this, if I did not feel that the subject is really before those, who are most competent to judge of it, in a somewhat imperfect form; that I have as yet offered to the chemical world the first part only of the method of which I am about to speak; and that this method will be much better comprehended, both from a mathematical and chemical point of view, when you have before you the subsequent parts which I hope to present hereafter.

I am to speak of a method of representing the facts of chemistry, which is fundamentally different from the method at present in use. Let me say a few words upon the past history of chemical theories.

I believe that theory is essential to the existence of chemistry. The birth of the science was inaugurated by the construction of a definite theory of chemistry—the first theory which had ever been proposed, and which sought to give a definite and rational account of the facts of the science. This theory was the once world-famous doctrine of Phlogiston. In this theory the facts of chemistry were explained by the agency of a subtle, hypothetical, all-pervading principle, by the transference of which, from one chemical substance to another, it was assumed the facts of chemistry were correctly accounted for. It is easy, from our present point of view, to pass critical remarks upon the doctrine of Phlogiston, but it is not quite so easy really to comprehend that doctrine, and to put ourselves in the position of those great chemists who worked and who studied through its agency. If ever anyone was tempted to speak slightly of the doctrine of Phlogiston, let him remember that through the instrumentality of this doctrine the great discoverer of chlorine, the chemist Scheele, worked. Let him remember that the exact mind of Cavendish was contented with this doctrine. Let him remember again that the illustrious Priestley, that transcendently inventive genius, in posses-

sion of this doctrine, made the great discovery of oxygen; and that not only was he then content with this doctrine, but that he died a firm believer in and adherent to it. However, the doctrine of Phlogiston, like many human things, was destined to pass away,—Lavoisier shattered Phlogiston. For no inconsiderable period after this, chemists appear to have worked, if I may so say, without a theory; that is to say, that, as during the long alchemical ages chemists were occupied in collecting together those facts which were afterwards to be embodied in the theory of Phlogiston; so for a period of above thirty or forty years—that is to say, from the time of Lavoisier to the time of Dalton—chemists were employed in collecting together that exacter system of facts which was to form the basis of a far wider, a far more comprehensive, and a far nobler theory, namely, the great atomic doctrine. However, Davy appears to have worked and to have made his great discoveries without a theory. Davy never admitted the atomic theory, but rested content simply with the facts of numerical analysis.

In the year 1808 there appeared that famous book, “A New System of Chemical Philosophy,” which contained the germs—indeed, I may say, almost the full development—of the atomic theory itself. In this atomic doctrine Dalton took up the conception of combination, which was introduced into the science by means of the theory of Phlogiston. He took up that doctrine of combination, and moulded it into a new and a more definite form. It would be useless for me, before the Chemical Society, to dwell upon the atomic theory. It is a theory with which every one is familiar, for every chemist of this day has worked with that theory, has conceived his science from the point of view of that theory; and, indeed, I believe it is, in the opinion of many, almost impossible that that doctrine should ever fall to the ground. This doctrine of Dalton, however, was a doctrine far more audacious than that of Stahl. In the theory of Phlogiston, Stahl considered that he had palpable evidence of the transference of his Phlogiston from chemical system to chemical system; but Dalton told us that this notion of the continuity of matter—that obvious fact which our senses teach us—was simply an illusion of the senses, and that, if only we could see things aright, we should see that this world, which appears to us so connected and so continuous, was really made up of an almost infinite number of disjointed fragments.

From the point of view of the atomic theory, I say, chemists have worked for a period now of about sixty years, and the progress of chemical theory has consisted in the almost constant and unremitting development of this doctrine. I cannot say, however, that this has been an unremitting progress. It has rather been a succession of events. System has followed system, doctrine has followed doctrine; but these doctrines have, one after another, fallen to the ground. We have had but little that is permanent, and at the present moment the theory of chemistry is built upon the ruin of other theories. Now, no one can have more respect, or more admiration for these great ideas, which were thus ushered into the science by Dalton, than I myself have. It cannot be necessary for me to express to this Society the admiration which I feel for that theory; but, nevertheless, I cannot but say that I think the atomic doctrine has proved itself inadequate to deal with the complicated system of chemical facts, which has been brought to light by the efforts of modern chemists. I do not think that the atomic theory has succeeded in constructing an adequate, a worthy, or even a useful representation of those facts. I say that for sixty years the united efforts of chemists, including many of the most able men in the world, have been devoted to the development of this doctrine, and they have formed their representations upon this doctrine. Now, let me read to you an account of the last modern representation of the atomic doctrine, and the chemical symbols

in which the atomic doctrine has resulted. I will read to you a paragraph headed “Glyptic Formulæ;” it is given in a scientific journal. Here is the paragraph:—

“Those teachers who think, with Dr. Frankland and Dr. Crum Brown, that the fundamental facts of chemical combination may be advantageously symbolized by balls and wires, and those practical students who require tangible demonstration of such facts, will learn with pleasure that a set of models for the construction of glyptic formulæ may now be obtained for a comparatively small sum.” (Much laughter.) “At first sight, the collection of bright-coloured and silvered balls suggests anything but abstract chemical truth,”—

And so on. However, I will tell you what you may get for your money:—

“There are seventy balls in all for the representation of atoms—monads, dyads, triads, tetrads, pentads, and hexads, being distinguished by the number of holes pierced in the balls. To connect these into rational formulæ”—[which, I confess I should think was a truly difficult problem]—“brass rods, straight or bent, and occasionally flexible bands are employed.” (Laughter.)

And so on. However, the editor seems to have had some misgivings, for he proceeds to say,—

“Whether they are calculated to induce erroneous conceptions is a question about which much might be said.”

Now, however much might be said upon this subject, I certainly am not going to say a great deal to the Society upon it; but it is truly a remarkable fact, that the atomic theory, after so many efforts, has resulted in such a symbolical representation as this. I think that great injustice is done in connecting the names of Dr. Frankland or of Dr. Crum Brown specially with such ideas as these, for I cannot but say that I think the promulgation of such ideas—even the partial reception of such views—indicates that the science must have got, somehow or another, upon a wrong track; that the science of chemistry must have got, in its modes of representation, altogether off the rules of philosophy, for it really could only be a long series of errors and of misconceptions which could have landed us in such a bathos as this.

You may, however, ask me, and with reason, “In what way, then, are we to represent the facts of chemistry, if we are not to represent them in this way? Do you mean to deal with this complicated system of facts, and to offer us no mode of representing these facts, and no mode of conceiving these facts?” Now, I certainly believe that any person who seriously attacks these ideas, is bound to show some other, and, I will say, some better way of representing the facts. I think he is bound to do this, or he should refrain from his attacks. You ask me, how we are to represent the facts of the science. It is to that question that I wish to offer an answer to-night.

I say that we are to express the numerical facts of the science by means of symbols; but I attach to the term “symbol” a very special signification. We have plenty of what are called “chemical symbols” already; but these chemical symbols are not, from my point of view, symbols at all, and you will presently see why. Not only according to my ideas, but according to the ideas of most persons who consider this question, a symbol may be regarded as a mark by which we express the objects of our thoughts for the purpose of reasoning about those objects; and one which is capable of being combined with other similar marks according to certain definite laws of combination; which laws of combination are to be possible, through the interpretation of the symbol, in the subject matter which is symbolized. That is what I mean by a symbol.

You will readily see that our present notation really can hardly be called, even in courtesy, a symbolic representation. The reason is, in the first place, that these letters

are not capable of being combined with other letters, or other marks, according to any definite laws at all; and, in the second place, so far are they from having any definite signification or meaning attached to them, that every chemist thinks himself at liberty to deal with them just as he pleases, according to his fancy. Now, I say, I wish to put a restriction upon that mode of dealing with the subject, and to bring my fellow chemists and myself under some definite laws when they deal with symbols.

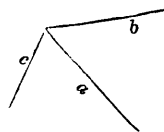
Symbols are of two kinds. We may have symbols of things, and we may have symbols of operations. Symbols of operations are simply symbols of what we do to things. Take a popular case; ordinary language is an imperfect symbolic system, and here we have just these two kinds of symbols. A "dog" is the symbol of a thing, and "beating," "caning," "coaxing," and so on, are the symbols of operations, or of something which we may do to a dog. We have marks by which we express things, and marks by which we may express what we do to things. We might also have a third kind of symbol; we might have the symbol of an operation and a thing together. Thus, if we did not wish to represent particularly what sort of animal we were going to beat, we might have a single mark for "beating an animal;" the thing and the operation being included in one.

I purpose, however, to go into a more exact kind of symbolism; but before I commence my explanations, I should like to remove one or two popular errors upon this subject. I believe there is no error more ingrained in the popular mind than that these marks $+$ $-$ \times $=$ are the symbols of adding, subtracting, multiplying, and identification or equalization; I mean that these marks are purely arithmetical symbols, and are to be used for the purposes of arithmetic alone, and that in any other subject matter to which they are applied it is essential for us to give these symbols their arithmetical signification. If that were true, the application of symbols to the science of chemistry would simply be, from my point of view, an impossibility.

Perhaps I shall best illustrate this matter, if I give you from another subject, an example of the mode of constructing a symbol, and what we mean by a symbol. It is an example which will bring before you clearly how independent symbols are of their arithmetical meaning or interpretation. I say of their arithmetical meaning, not of their arithmetical laws, which is another thing. In ordinary algebra we denote, by the mark a , the operation of conferring upon the unit of length a certain length which we designate as a . This length we may call three feet, and the mark a will thus stand for a line three feet long. Now, if we take another symbol, b , that may indicate to us a line drawn in the same direction as a , but of another length. We will say that b is five feet. Now a tells us that we are to draw a line of a certain length; and we may say that the symbol $+a$ means that we are to draw it in a certain direction. Now if we ask what is the meaning of $+a+b$, this indicates to us that, having drawn a , we are to start again, and we are to draw another straight line of the length of five feet, which we call b . Or, in ordinary geometry, $+a+b$ would symbolize to us a line, the length of which was the sum of the length of a and b , and drawn in the same direction.

I wish now to bring before you, very briefly, an illustration of how totally unnecessary this arithmetical application of the meaning of the symbol $+$, is to its algebraic meaning. We have another kind of geometry, we may say, in which the symbols a , b , c , and so on, may indicate to us not only length, but direction also; so that if we take a certain point as our starting point, the symbol $+a$ would indicate to us that we were to start from the point a and draw the line $+$ in a certain direction,—we will say towards the horizon. And b would indicate to us that we were to draw a line in another direction, and of

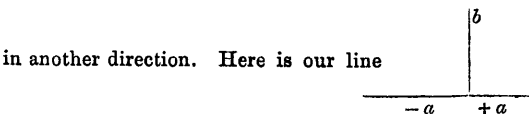
another length; and c that we were to draw a line in a third direction, and also of another length. Thus



in short, it is open to us, if we choose to do so, to express by letters, not magnitude only, but also position.

Now, I wish you simply to see at what we arrive by following out these principles. What is the interpretation of $a+b$? a tells me to draw a line from our starting point in a certain direction and to a certain length. $a+a$ indicates that I am to make a line in the same direction as a and twice as long; in like manner $-$ would also indicate to us the direction in which we were to draw our line relatively to the starting point. $-a$ would be a line equal in length to a , but in the opposite direction to $+a$.

Now b tells us that we are to perform upon the unit of length an operation which is to consist in drawing a line



in another direction. Here is our line

What therefore do we mean by $+a+b$? Why $+a$ tells us that we are to construct the line a . And having done that we are to go on again and construct b . That is done by beginning again at the end of the line a , and drawing a line in the direction of b , and equal in length to it, by

which means we get

If we draw the diagonal of

the parallelogram of which a and b are the sides, the diagonal of that parallelogram is expressed, and properly

expressed, as $a+b$

And I say that a line drawn

through the first point, equal in length to the other diagonal of the parallelogram but in the opposite direction, is

properly represented by $b-a$

Those two

diagonal lines in the system of geometry express $a+b$ and $b-a$. The reason of this you will perceive is very obvious, for, as we all know, the diagonal line, relatively to direction and to the motion which makes it, would be the same in kind and in quantity as the motion which constitutes the lines a and b . In short, we first of all construct the line a , and then we go on again and take up the line b . The diagonal of the parallelogram is therefore properly expressed as $a+b$, but of course this diagonal is not equal in length to the sides of the parallelogram.

There is one other property I must refer to, which is very important, and comes out to us in the symbol $+$. It is, that $a+b$ is the same thing as $b+a$. Why is this? It is simply that when we go along the line in direction a , and then travel through the length of b , we arrive at the same quantity as when we go along the lines $b+a$.

In constructing any calculus or method, then, the principle to be observed, in regard to the symbols, is by no means to give to them their arithmetical meaning or interpretation, but simply to construct them properly according to the laws which they obey in arithmetic and in algebra.

To take another example, using the marks + and - as the simplest illustration. They may be regarded as marks which are subject to a certain system of laws, which laws are given in the following equations:—

$$\begin{aligned} + + &= + \\ + - &= - \\ - + &= - \\ - - &= + \end{aligned}$$

If, then, you can find in any subject matter, any properties to which you may apply these symbols + and - consistently with this interpretation, I think you are justified in using the symbols + and - to express those properties.

Let me proceed to explain, very briefly, what I mean by a chemical symbol. The object, I should say, of the first part of this method is to discover a proper system by which we are to express the unit of chemical substances. I may put this in another way, and say that we wish to discover what is the nature and the number of the operations by which chemical substances are made or constructed. That is the first object of our method. I should, perhaps, limit myself a little farther, for I should say that before we begin to think about chemical substances at all we should conceive of them as all brought into the condition of perfect gases. Now, the reason of this is one which I am sure will commend itself to every chemist: it is the simplicity of the laws to which gaseous combinations are subject, which simplicity was first discovered by the great chemist Gay-Lussac. Of course we may deal with the properties of the combinations of solids and liquids, but here it is far more difficult for us to arrive at any intelligible and simple results; and, whether rightly or wrongly, before beginning to think about the nature of a chemical substance, I, for my part, always conceive it as brought into the condition of a gas. And to go a little further, and to speak a little more definitely, we shall always consider the chemical substance brought into the condition of a gas, at the temperature of 0 degrees, and at a pressure of 760 millimetres. This is the sort of ideal chemical world with which we have to deal. It is a world of gases.

First let me indicate to you the definition which I will take of a unit of matter; for it is absolutely essential, before we think about matter at all, to begin with defining the unit which we are about to consider. That definition is of such great importance that I have had the words placed up before you in this diagram.

The unit of ponderable matter, is that portion of ponderable matter, which, at a temperature of 0 degrees, and at a pressure of 760 millimetres of mercury, occupies a space of 1000 cubic centimetres.

From considering the unit of matter, I pass now to the consideration of a unit of another kind, and that is what I call the unit of space—that is, the volume of 1000 cubic centimetres. And just as, before we begin to think about chemical substances, we must bring them all theoretically to the state of gas; so, before beginning to think about the unit of chemical substances, we must begin by thinking about a unit of space. This is the fundamental conception of this method; and it is a notion which appears to me to be almost essential to any constructive chemistry at all—that is, the conception of the unit of space; let us, therefore, clearly understand what the unit of space means. Now, that there may be no doubt about it, I have brought you the unit of space [exhibiting a hollow cube with glass walls, and of the dimensions above assigned to the unit of space].

You have to do something else, however, before you get the unit of space. It is indeed the space of 1000 cubic centimetres which is confined within these glass walls; but before you can get at the unit of space, you have to go a step farther, and by the process of imagination, or by the efforts of reason, you have to divest this cube of glass of weight, and take out of it all the ponderable

matter which it contains, and conceive the space within the walls divested of matter altogether. Now, this unit of space is so fundamentally important to us that I shall begin by giving it a mark to itself. The mark which I give to that unit of space is, for certain good reasons which I will not explain now, the mark \mathbf{x} . When you see that mark, it is to recall to your mind the matter contained in the unit of space. Now, what is that matter? Why, that matter is simply no matter at all; there is no ponderable matter in it.

Perhaps, however, if I were to speak a little more exactly and precisely, I should say, for the benefit of those persons who may be more philosophically inclined, that the mark \mathbf{x} is the symbol of the operation of taking the unit of space as it is. That is, take the unit of space as it is, and do nothing at all with it.

However, we must not only consider units of space, the consideration of which alone would lead us to very little, but we are going to consider the units of matter. Now, how are we to conceive a space becoming matter, or of matter getting into space—chemically, I mean? Well, I shall think of this through the aid of an operation, and I shall define by a mark the operation by which this empty unit of space is turned into a unit of ponderable matter. For example, I will take \mathbf{z} as such a mark. This is the mark of the operation by which the unit of space becomes a unit of ponderable matter. It is the mark of a certain density which is appropriated to \mathbf{z} , and of a certain kind which is also supposed by \mathbf{z} . Here, then, is \mathbf{z} , the symbol of the operation; and how are we to symbolize the performing this operation upon the unit of space? I shall do this in a natural manner by writing the letter \mathbf{z} before the unit of space, \mathbf{zx} ; and that indicates to me matter of a certain density, and at 760 millimetres pressure.

How are we now to conceive of matter, double the density, but the same in kind as \mathbf{z} ? Having once conferred upon the unit of space this density, we have only to perform the operation a second time. Hence, to double the density, we have only to write \mathbf{z} again, thus: \mathbf{zzx} . This will symbolize that we confer on the unit of space a certain density, and having done that we confer that density on it again. That is, we make it double the density. \mathbf{zzzx} will mean that we give it three times the density. We can abbreviate the expressions. We need not write the \mathbf{z} 's out at length. The unit of space is \mathbf{x} ; with the first density conferred upon it, it becomes \mathbf{zx} ; with double the density, $\mathbf{z^2x}$; and with three times the density, $\mathbf{z^3x}$. If you compare these operations with the symbols which express the densities, you will see that the symbols of the units of matter which we have thus constructed, stand to the numbers which express the densities of that matter, in the same relation as numbers do generally.

We will now take another kind of matter: \mathbf{y} , $\mathbf{y^2x}$, $\mathbf{y^3x}$. This, again, would be a symbolized ponderable matter which would be contained in this glass box at the pressure and temperature indicated, of the kind indicated by \mathbf{y} , and of the density indicated by the number of units of \mathbf{y} . You will see this more obviously when we come to speak of the symbols of chemical substances.

If we proceed farther upon the same principles, we come to consider what is the symbol of units of space containing two kinds of matter. Well, on the same principles, you see, we have \mathbf{zyx} as the symbol of the unit of space filled with the matter of \mathbf{z} , and also filled with the matter of \mathbf{y} ; that is to say, having the density \mathbf{zy} , the sum of the densities of \mathbf{z} and \mathbf{y} . And of course we can, in this way, symbolize also the unit of space filled with the matters \mathbf{z} and \mathbf{y} in various proportions.

You will see that there is a real analogy between the symbols which I am here employing, and the symbols which I used just now in my illustration derived from double algebra; for just as the symbols of double

algebra indicate to us not only the length of a line, but also its direction or position, so these chemical symbols indicate to us not only the weight, but also the kind of matter. You are not to confound them with the numbers which express the densities, or the letters by which we might express those numbers; but they are, I say, symbols which express to us, at one and the same time, the nature of the matter and the density of the matter, having a double signification of this kind.

Before we go further, let me say a word about the nature of this operation. I am here symbolizing the unit of matter by the symbols of the operation by which the unit of matter is made. But what is that operation?

Well, speaking generally, I may say, without entering into too nice logical distinctions, that it is an operation which every chemist knows better than any other physical operation. It is the operation of combination. That is what x is, and what y is. They are operations of combination. We are getting thus at a definition of our unit in terms perhaps more in accordance with our ordinary language. We will call the matter of x , A, and the matter of y , B; and the matter of the unit of space, merely o . That is always definite. What, then, does x stand for, considered from the point of view of combination? It is the operation of combining the matter A with any substance which we please to write after the symbol of the letter. Similarly, y is the symbol of combining the matter B. Then we may call i the symbol of no matter; it is the symbol of the unit of space, which has no matter. xi tells us we are to take A, and combine it with the matter of the unit of space. The result of that is to constitute the matter A. Having done that, I write y to it (xyi). That tells me to take the matter B and combine that also with the matter of the unit of space. If you do that, the result is the matter of A combined with the matter of B. These are the operations. Do not imagine there is anything mysterious about these terms. They are the operations about which you think every day of your life; and, I say, if you want to think philosophically about chemistry, you must embody in your symbol the very thing which you are thinking about, namely, the operation of combination itself.

I must not seek to explain to you now the process or method by which we arrive at the symbols of chemical substances, for to explain the process on the board, and to do it any justice, would occupy far more time than is at my disposal. You must allow me now simply to explain what we mean by the symbol of chemical substances (I mean in special cases), and then to consider the general results to which this mode of representation conducts us.

As to the mode of constructing these symbols, it is based in the most absolute way upon facts. We do not construct a symbol at all. We simply look for the symbol of matter and we find it. Where are we to look for the symbols of a chemical substance? Why, plainly to the symbols of matter in the gaseous condition: and where are we to look for the symbols of the operations by which units of matter are made? Why, plainly in the facts of combination. That is the source whence you are to deduce the symbol: it is the fact of combination itself. The facts in gaseous combinations are such as these:—2 volumes of hydrochloric acid consist of the same ponderable matter as 1 vol. of hydrogen and 1 vol. of chlorine. 2 vols. of gaseous water consist of the same ponderable matter as 2 vols. of hydrogen and 1 vol. of oxygen. Again (I will now put it in my way), 2 units of ammonia consist of the same ponderable matter as 3 units of hydrogen and 1 unit of nitrogen. These are the facts, and chemistry supplies us with a vast, but not an infinite number, of such facts. The method which I have ventured to give is simply a method of expressing the facts of the equation in the symbol of the substance. It is simply and purely a method of taking an equation, and of embodying in

the symbol the facts of the equation. Through the facts of the equation we construct the symbols of the units of ponderable matter. We then take the symbols out of the equations, and we thus separate and analyse the facts one from the other. It is simply an analysis of facts of a peculiar kind.

I have constructed some tables expressive of the general nature of the conclusions, at which we arrive through the aid of this method, as to the composition of these units of matter. I have had a good many of these symbols written out, for really it is easier for you, by looking at these tables, to see the general results which we arrive at by this method, than it would be for me to enter into a long explanation of the process. Here you see are the symbols of the chemical substances. We start with the symbol of the unit of space.

Symbols of the Units of Chemical Substances.

Unit of space	i
Hydrogen	a
Oxygen	ξ^2
Water	$a\xi$
Peroxide of Hydrogen	$a\xi^2$
Sulphur	θ^2
Protosulphide of Hydrogen	$a\theta$
Bisulphide of Hydrogen	$a\theta^2$
Sulphurous Anhydride	$\theta\xi^2$
Sulphuric Anhydride	$\theta\xi^3$
Sulphurous Acid	$a\theta\xi^3$
Sulphuric Acid	$a\theta\xi^4$
Chlorine	$a\chi^2$
Hydrochloric Acid	$a\chi$
Hypochlorous Acid	$a\chi\xi^3$
Chlorous Acid	$a\chi\xi^2$
Chlorosulphurous Acid	$a\chi^2\theta\xi$
Hypochlorosulphurous Acid	$a\chi\theta\xi^3$
Chlorosulphuric Acid	$a\chi^2\theta\xi^2$
Iodine	$a\omega^2$
Bromine	$a\beta^3$

In the next table is another system of symbols, those of the combination of carbon, hydrogen, and two or three other elements.

Carbon	κ^2
Acetylene	$a\kappa^2$
Marsh Gas	$a^2\kappa$
Olefiant Gas	$a^2\kappa^2$
Carbonic Oxide	$\kappa\xi$
Carbonic Acid	$\kappa\xi^3$
Alcohol	$a^2\kappa^2\xi$
Ether	$a^2\kappa^4\xi$
Glycol	$a^3\kappa^2\xi^2$
Glycerine	$a^4\kappa^3\xi^3$
Anhydrous Acetic Acid	$a^3\kappa\xi^3$
Tetrachloride of Carbon	$a^2\chi^4\kappa^2$
Chloroform	$a^4\chi^3\kappa$
Chloroacetic Acid	$a^2\chi\kappa^2\xi^2$
Trichloroacetic Acid	$a^2\chi^3\kappa^2\xi^2$
Chloride of Benzoyl	$a^2\chi\kappa^4\xi$
Cyanogen	$a\nu^2\kappa^2$
Hydrocyanic Acid	$a\nu\kappa$
Methylamine	$a^2\nu\kappa$
Mercuric Ethide	$a^2\kappa^2\delta$

You must regard these symbols as being chemical equations turned into another form, and divested of a certain amount of superfluous and useless matter, which we do not want now to consider or think about. Nature does not supply us with the key note to enable us to construct a definite system of chemical symbols. Nature does not tell us absolutely—though I think she does tell us probably—how we are to proceed to construct a system. In order to be able to construct a chemical system we must start with a hypothesis of some kind or other. As we go on constructing our symbols, of course our hypothesis, as we prove it, becomes a fact; but we must,

at any rate, start with some hypothesis; that is to say, we must know one symbol. We may construct a complete chemical system from one symbol; and we may view all these symbols as taken from one hypothesis, combined with the facts given to us and supplied by the equation. Now, that hypothesis is this, that the symbol of the unit of hydrogen is expressed by one letter, α . That is my starting point; and I should say that the symbols which you see in the tables, as indicating chemical operations, are regarded as symbols of primary operations, that is to say, operations which you cannot resolve or decompose into any other symbols.

They are symbols of the primary operations; and when I say that the symbol of hydrogen can be expressed in chemical equations by one letter, I mean that in the changes and transformations of chemistry that unit of hydrogen is never broken up; that it moves as a whole from system to system, and that that unit of hydrogen is never decomposed or resolved into parts. The unit of hydrogen is constructed at once, by one operation. What I mean is this: imagine yourself witnessing the formation of hydrogen. To form some substances you want many operations; but to form hydrogen you want only one operation. That [striking a blow on the glass model of the unit of space] represents the formation of hydrogen,—one operation. It is one act. If we could witness chemical transformations, and nature would only become vocal to us, and indicate each combination as it occurred, by a musical note, that [again striking a blow] is what you would hear when hydrogen was formed. Now, as we go on we come to much more complex substances. Let us take oxygen. This is a substance very different indeed from hydrogen in its chemical properties; and as you can conceive of the unit of hydrogen being made at once by one operation, I say that it is impossible for you to conceive of the unit of oxygen being made by less than two operations. To return to our metaphor, when you take water and decompose it, and when you hear the oxygen go away, you ought to hear two notes, like this, [striking two blows in close succession.] That is what I mean by saying that oxygen is made by two operations. Again, the unit of water is made by two operations like the unit of oxygen; but it differs from the unit of oxygen in this respect, that one of those operations is the same as that by which hydrogen is made, and the other is the same as that by which oxygen is made. That is to say, in the operation by which water was formed, you would hear two sounds, one different from the other, α , ξ .

The symbol of chlorine is $\alpha\chi^2$. Chlorine, from this point of view, is to be conceived as made up of three operations. You are to hear χ , χ , and then α again. One of these operations is the same as that by which hydrogen is made, and the other is an operation peculiar to chlorine itself, namely, χ . Again: a unit of hydrochloric acid—a thousand cubic centimetres, in the condition of a perfect gas at a pressure of 760 millimetres—is to be conceived of as made by two operations, $\alpha\chi$.

To go one step further: let me refer you to this table:—

Nitrogen	$\alpha\nu^2$
Ammonia	$\alpha^2\nu$
Protoxide of nitrogen	$\alpha\nu^2\xi$
Nitrous acid	$\alpha\nu\xi^2$
Nitric acid	$\alpha\nu\xi^3$
Phosphorus	$\alpha^2\phi^4$
Phosphide of hydrogen	$\alpha^2\phi$
Hypophosphorus acid	$\alpha^2\phi\xi^2$
Orthophosphoric acid	$\alpha^2\phi\xi^4$
Terchloride of phosphorus	$\alpha^2\phi\chi^3$
Pentachloride of phosphorus	$\alpha^3\phi\chi^5$

Nitrogen is to be conceived of here as made of three operations, $\nu\nu$, and then α upon that. In the formation of the unit of ammonia three operations concur. One of them being one of the operation of nitrogen, ν , and the

other two being the operations by which hydrogen is formed, α .

I must not enter into further details upon this subject, but I have little doubt that, with this explanation, you will readily appreciate the meaning of the symbols which are written up before you. You will see that, by following this process of taking the facts of the equations and turning them into the language of symbols, we arrive at a peculiar view as to the nature of matter, which view is embodied in those symbols.

Now, as to the nature of the view which is here indicated, for that, perhaps, will occur to most persons, as the most important point to be considered. This view is the only result which I have placed before you, in the first part of this method. It is the view as to the nature of matter itself. You will observe that, looking simply from the general point of view of the nature of matter, the point which it is most important for us to insist upon is the nature of the elemental bodies, because it is out of these elemental bodies that everything else is made, and into them all things are capable of being resolved. The view which we take of these bodies gives to us implicitly the view which we are to take of the composition of every other body whatever. To understand this it is only necessary to appreciate the view which is here given of the nature of the elements themselves, and everything else follows from that. We are led to the following singular results,—that, speaking generally, there are, perhaps, four—certainly at least three—fundamentally distinct classes of the elemental bodies.

First of all, there are elemental bodies, the units of which are made by one indivisible operation. These bodies are represented to us by mercury and hydrogen. To this class also probably belong such elements as zinc, cadmium, and tin; but we cannot speak with great confidence on that point.

Secondly, we have a class of double elements, formed by two similar operations, these are oxygen ξ^2 , sulphur θ^2 , selenium λ^2 . Carbon we are not certain about, it belongs, in all probability, to the first or second class, we do not quite know which; but I have symbolised it as κ^2 .

But we have another and a very large class—perhaps the largest of all the groups of the elements—and we may take the elements chlorine and nitrogen as representatives of it. Here is the symbol of the element chlorine, $\alpha\chi^2$; here is nitrogen, $\alpha\nu^2$; here is iodine, $\alpha\nu^2$; and so on. You will see that the symbols of these elements occupy a certain intermediate position between this group of elements, α , δ , ζ , &c., and that group of elements, ξ^2 , θ^2 , λ^2 , &c. We have many compound substances which are in every way analogous to this group of elements—analogous as to their properties, analogous as to their symbols. Of this class we have a most interesting and striking example in the peroxide of hydrogen; it is symbolized here as $\alpha\xi^2$. You see the peroxide of hydrogen is really to be regarded as the combination of one unit of the element hydrogen with one unit of oxygen—which things really exist—just as the element chlorine may be regarded as a combination of the unit of hydrogen (α) with a substance which does not exist, and which I have symbolized as χ^2 . The unit of nitrogen is to be regarded as similarly composed ($\alpha\nu^2$). We may regard it as a combined with the unknown element ν .

There is one question which must occur to every one, the explanation of which is of fundamental importance to the comprehension of this system. You may ask me, "What do you mean by these symbols—by calling chlorine $\alpha\chi^2$; nitrogen, $\alpha\nu^2$; oxygen, ξ^2 ?" Do you mean that there are certain portions of matter, really existing, capable of being brought to the lecture-room—theoretically, at any rate—and shown upon the lecture-table: portions of matter which are represented by α and χ , α and ν , and so on? Do you mean this? or do you mean that these things are the creations of your imagination—that they are fictions—illusions? We like," perhaps you

may say to me, "we like Dalton a great deal better than we do you; for Dalton, at any rate, dealt with realities, or possible realities. He, at any rate, showed us the matter of which all substances are made. He brought the elemental bodies into the lecture-room in bottles, and he showed us there the elements out of which matter is made. Are you going to do that? Do you mean to show us α , ξ , χ , in the lecture-room? Again, Dalton dealt with realities through these atoms. Although, certainly, we have never seen them, yet, nevertheless, we most perfectly believe them to exist. There are such things as atoms, although we have never seen them. Dalton brought the elements to the lecture-table; and if he did not actually show us the atoms, you will find pictures of them at the end of his book;—he made little bits of wood which were excessively like atoms, although they were wood. But you don't even do this for us." Well, this is rather a perplexing question; for if you ask me if these things really exist—whether they are things capable of being brought to the lecture-table and placed before us—in answer to such an enquiry I say, in the first place, that they do not necessarily exist. Then, again, you ask me this: "Do you say that they are imaginary things; that they are creations of your fancy? Because, if so, we don't trouble ourselves much about your fancies. They are not worth thinking about." I say, no, they are not fancies of mine; I never made them? I only found them. Then you answer: "All things are either imaginary or real: which are these?" Well, I reply, these things are *ideal* things. Well, then, my friend says I am getting beyond him when I say these are ideal, for he does not understand what ideal things are: all things are either imaginary or real. Yes; but I say there is a point which you have overlooked. Either all things exist according to the laws of nature which make it possible for them to exist, or there are insuperable barriers in the laws of nature to their existence. But though we may not know whether certain things exist or do not exist, yet we may reason about these things as if they were real things. A thing may not exist at all, but yet it may serve to us all the purposes of a real thing. That is what I mean by an ideal thing. It is a thing which may exist or may not exist, we do not know which, but which satisfies all the conditions of reality.

I shall venture, at the risk of delaying you a little longer, to give you an illustration on this point, which was suggested to me by some remarks and illustrations of Professor Stokes, with whom I have had the, to me, incomparable advantage of discussing and considering several of these difficult and abstruse questions. My illustration is simply his illustration a little modified for you. I am going to make a general assertion. I will draw a conic section—a curve—on the board, and I am going to say that every straight line cuts every conic section in two points. That, you see, is somewhat analogous to my statement, that the unit of every chemical substance is composed of an integral number of prime factors, and is to be regarded as made up of an integral number of these bits of matter which I call symbol weights. There are the two corresponding assertions. But you say, "Do you mean that every straight line really cuts the conic section in two points?" I say, no, I never said that it *really* cut it at all. I said it *cut* it. Then you say, "Do you mean that it cuts in imagination?" I say, no, I do not say this. I do not know whether the line cuts it in reality or in the abstract. I do not know, speaking generally, whether the points at which a straight line cuts a conic section are real or imaginary. They are one or the other. You see that is a perfectly general mathematical truth and principle. Nothing is easier than to prove any proposition; and I may go on to say, that in the case of a straight line, of course, we can go farther: we can investigate the nature of these points; we can determine the nature of these

points. But in chemistry we come to a bar. We cannot go on. We have not yet got the data to prove whether these prime factors, these units of weights are real things or imaginary. They are undoubtedly one or the other, but we cannot tell which. There are facts here which satisfy all the analytical conditions of the facts, whether the matter is real or imaginary. There are symbols of facts which satisfy the analytical conditions supplied to us by the equations of chemistry, and as such we are bound to accept them. We cannot do otherwise. It is impossible for us not to accept the conclusion.

We cannot, however, entirely dismiss from our consideration the alternative that these portions of matter— α , χ , ξ , ν , and ω , may be real. I mean a real thing when I say "a real thing." I mean something which may be brought to the lecture table and put there, really or theoretically. We cannot close our eyes to that alternative; and there really are, though not at all derived from this method itself, but derived from other considerations, certain real reasons which would lead us to suspect that chemical substances are really composed of a primitive system of elemental bodies, analogous in their general nature to our present elements, some of which we possess, but of which we possess only a few. I will take the case of the peroxide of hydrogen. I will throw overboard oxygen and a great class of certain oxygenated combinations, and I will suppose for the moment that I have these combinations—hydrogen, water, peroxide of hydrogen, and certain other substances which I could specify. If I were to apply my method to finding the symbol of peroxide of hydrogen, not regarding the oxygen at all, the symbol at which we arrive for peroxide of hydrogen is $\alpha\xi^2$. Thus the same question would arise in that case about peroxide of hydrogen as now arises about chlorine. In peroxide of hydrogen we really have succeeded in separating the elements which it contains, and this fact leads us to the suspicion that some of these bodies which we speak of as elements may in fact be compounds. In short, we are led, through our method, to a certain physical hypothesis, of whatever value that hypothesis may be, as to the origin and causes of chemical phenomena.

Now, what I am going to suggest is of course put before you with reservation, but we may conceive, that, either in remote time, or in remote space, there either did exist formerly, or there do exist now, certain simpler forms of matter than we find upon the surface of our globe— α , χ , ξ , ν , and so on—in short, these symbols of chemical operations. I say we may at least conceive of, or imagine, the existence, either in time or in space, of these simpler forms of existence, of which we have some records remaining to us. Here they are—hydrogen and mercury—two things. We may consider that in remote ages the temperature of matter was much higher than it is now, and that these other things existed then in the state of perfect gases—separate existences—uncombined at any rate. This is the farthest barrier to which we can reach. There may be something farther, but if so, we can have no suspicion of it from the facts of the science. We may, then, conceive that the temperature begins to fall; these things begin to combine with one another. They enter into new forms of combination, appropriate to the circumstances in which they are placed. The result is the formation of new combinations. We may suppose that at this time water ($\alpha\xi$), hydrochloric acid ($\alpha\chi$), and many other bodies, began to exist. Now, we may further consider that, as the temperature went on falling, certain forms of matter became more permanent and more stable, to the exclusion of others. We have evidence on the surface of our globe itself, of the permanence of certain forms of matter to the exclusion of others. We may conceive of this process of the lowering of the temperature going on, so that these substances, $\alpha\chi^2$ and $\alpha\nu^2$, when they were once formed, could never be decomposed,—in fact, that the resolution of these bodies into their component elements could never

occur again. You then have something of our present system of things. You might yet imagine that it would be possible, on looking carefully at chemical equations, and minutely studying them, to recover from the equations the record of the truths which were buried and preserved in the equations; and some analyst might come and say, "These equations are *only* consistent with this hypothesis, that chlorine is composed of α and χ^2 ," or, at least, it might be said that the equations are consistent with that hypothesis, for I do not want to go farther than that. In short, we can conceive of such a state of things. Now, this is not really and purely an imagination, for when we look upon the surface of our globe, as I said before, we have evidence of similar changes in nature. We talk of the elemental bodies as though they were existing things; but where are they? We have oxygen, nitrogen, sulphur, certain metals, and certain bodies which we could specify, but what has become of the others? Where is hydrogen? Where is chlorine? Above all, where is fluorine? Where are these things? Why, they are at any rate locked up in combination, in such a way that it is only within the last hundred years that the art of the chemist has revealed them to mankind. Now, if in our globe there had been more hydrogen,—if there had been an excess of hydrogen present in the matter from which our globe was made,—and if we suppose it to be true that the gases condense in the solid matter of our globe, we cannot doubt that the whole of the free oxygen would have been carried away from our planet, and that we should have had simply oxygen stored up in the form of water. We should have had water, but no oxygen at all; all the hydrogen would have combined with it and carried it all away.

When we look at some of the facts which have been revealed to us, by the extraordinary analyses which have been made of the matter of distant worlds and nebulae, by means of the spectroscopic, it does not seem quite incredible to me that there may even be evidence, some day, of the independent existence of such things as these, χ and ν . We know that Dr. Miller and Mr. Huggins saw a most wonderful hydrogen combustion—at least, what they imagined to be a hydrogen combustion—taking place in a variable star. Now, for aught we know to the contrary, this hydrogen combustion might be merely hydrogen combining with unknown elements, and carrying them all away in the form of chlorine, nitrogen, and the like. One of the nebulae examined by Dr. Miller and Mr. Huggins afforded them the spectrum of an ignited gas, and in the spectrum of the nebula they saw one of the lines of nitrogen alone. Now, this suggests that this line might have been produced by one of the elements of nitrogen, before it had combined with another substance to form nitrogen. That might have been the element, ν . I am only suggesting that; but I say that if we follow up the subject we may have, one day revealed to us, independent evidence of the existence of these elements.

Let me, in conclusion, make one or two observations upon a point which, of course, must occur to every chemist who has studied this method. If we had taken, not α as the symbol of hydrogen, but had started with a different hypothesis, namely, that the symbol of hydrogen was α^2 , we should, of course, have arrived at a different symbolic system, that would have been analogous in its form to our present symbolic system—that is to say, you might have given to it an interpretation analogous to that system. We should have had hydrogen as α^2 ; water $\alpha^2\zeta$, and so on. In fact, we should have been led to develop a system different from that which I have brought before you. You may with reason ask me, "Why do you prefer one of these systems to the other; or do you prefer it; or what view do you take of that question?" Let me say, in the first place, that my object has been, hitherto at least, not to give you a very definite answer to this question. For I have not yet placed before you and others, the ideas upon which a judgment can properly be formed on the question;

but it is certainly true, in a certain sense, that there is more than one answer to the chemical problem, and that this system as thus developed, leads to another solution of the question. It gives you another answer to your inquiry. But further than this, there may be other answers still, although, perhaps, these are the only two answers necessary in considering the chemical problem; and this point which I wish to bring before you is of a far more subtle nature than it has been suspected to be. It is a method which you cannot attempt by the modes of atomic symbolism. It may be regarded as an equation of which there are not only one root, but several roots. Some of these roots may be thrown away, but some may lead us to a real solution. Now, I am not saying that one answer is the same in kind as the other answer, for I, with a natural preference, select the system α . I think there is something there, which is really of more importance and more necessary, in expressing the symbols than that which is given in the second system. I do not at all disregard that system. Indeed, I shall hereafter consider it, and endeavour to see, at any rate, what it means; but, I say, there is something in my system which is not in the second system—something in the system of α , which is not in the system of α^2 . I cannot discuss this question with the hope of producing conviction in your minds, but I will just point out one fact. It is this,—that you can pass from the system of α to the system of α^2 by a direct process of substitution. I mean, that if you say that here are two independent systems—the system of α , and the system of α^2 —I say those systems are not entirely independent; for if you have constructed the system of α , you can make a substitution of α^2 for all. What that system would be, it is not necessary here to imagine. But having constructed this system of α^2 , you cannot go back. It is not a logical consequence at all that, because you can take the square of the first system, therefore you can go back again. It will be absolutely impossible to pass at all from the latter system to the former. The one is derived primarily by substitution, and the other is not derived purely by substitution, but first by substitution, and then by reduction.

Discussion.

Dr. FRANKLAND: I am sure, sir, that I only express the feelings of everyone present when I say that I have listened to the lecture which Sir Benjamin Brodie has just given us with great interest and admiration. I cannot help thinking that the bringing forward of an entirely new method of viewing chemical phenomena such as has been brought before us to-night, must be fraught with great good to the science; but at the same time, I may be permitted, perhaps, having been alluded to in the earlier part of the lecture as a prominent advocate of what might be termed the opposite system of representing chemical facts, to protest at the outset, in the most emphatic manner, against the view which Sir Benjamin Brodie appears to have of such representations. I am not going to speak on behalf of other chemists who employ those more concrete modes of chemical representation. On my own behalf, however, in repudiation of the notion that I regard such representations as these graphic or glyptic formulæ, or even symbolic formulæ by letters only, in the sense of representations of the constitution of those portions of matter called atoms, or as representations of the position of these atoms in the compound; perhaps I cannot do better than state, simply and at once, that I neither believe in atoms themselves, nor do I believe in the existence of centres of force, so that I do not think I can be fairly charged with this very crude notion which would otherwise attach to me with regard to the representation of such chemical compounds. Now, sir, many people, I believe, have been much dissatisfied of late with chemical formulæ in one respect, and I confess that I am

one of the most dissatisfied. This note of dissatisfaction was, I believe, first expressed by Mr. Waterston. We do not express in our chemical formulæ, and in our chemical symbols, the idea of the *force* which has been involved in the operations expressed in those chemical compounds to which we apply the formulæ; and I think that one of the greatest advances which could possibly be made in the notation of chemical compounds, would be the introduction of this element. When, however, we leave statical formulæ—when we leave the mere representation of the atoms of compounds (if you will allow me figuratively, for a moment, to use the expression)—and when we go to the operations themselves by which those compounds are formed, I think we require then this expression of the forces involved, still more than we do in the statical formulæ that have hitherto been employed by chemists. Now, it appears to me, that we seek in vain for this element in the new development which Sir Benjamin Brodie has so eloquently placed before us this evening. Again, I think that every chemical formula is of use chiefly, if not only, as a means for future discovery in nature. So far as it serves that purpose it is of use, if it does not serve that purpose it is useless. The more, therefore, that a chemical formula expresses of our knowledge of the body for which we put it, the more valuable, I apprehend, that formula is. Now, if we take two well-known chemical compounds—namely, nitric acid on the one hand, and sulphuric acid on the other hand—I believe that if there is anything that we do know with certainty regarding these two acids it is this: that in the case of nitric acid the hydrogen present in that compound can be taken out of it in one piece only, whilst in the sulphuric acid you can take out the hydrogen in two pieces. Now, when I look at the formula of nitric acid az^3 , and of sulphuric acid az^4 , I find in both these formulæ the same expression for the hydrogen; so that, I say, there is not contained in that formula the same amount of information, and of the most essential information, with regard to these two acids, that we possess in the present formula, differ as they may amongst different chemists, and lamentably they do so differ; still, by almost every chemist those two acids are expressed by formulæ representing this peculiarity of the hydrogen in those two compounds. These new formulæ, I say, do not express that idea, do not give us that information. I certainly do not imagine that any evil is likely to arise from such symbolical representations as have been hitherto used, even those of the very crudest kind which have been so strongly censured by Sir Benjamin Brodie; and, further, I do not think that science would ever suffer from the legitimate use of hypothesis. In fact I cannot conceive of the future progress of science without such use of hypothesis; and I must say that it is to me a great recommendation for the new notation which has just been placed before us, that it involves a very fair amount of such hypothesis, which, I hope, will be capable of being used for the advance of the science, and for the benefit of its representations.

Professor CLEEK MAXWELL said he confessed that when he came into the room his feelings received a wholesome shock from two of the statements in the diagrams—first, that space was a chemical substance, and second, that hydrogen and mercury were operations. He now, however, understood what was meant. The present seemed to be an endeavour to cause the symbols of chemical substances to act in the formulæ according to their own laws. The formulæ at present used were made to express many valuable properties of chemical substances, just as a great many formulæ were employed to represent the syllogism in logic, which required a logical mind to form them, to understand them, and to reason upon them. The only successful attempt to introduce a new system in the logical representation was that of Mr. Boole, who accomplished it by the metaphysical and mathematical concep-

tion that x^2 was equal to x . In Sir Benjamin Brodie's system a did not mean exactly "hydrogen," but "make hydrogen;" that is, take the cubic centimetre of space, and put hydrogen into it of the proper pressure and temperature. But if they were to compress into that space another volume of hydrogen, that would not be α^2 , because it would increase the pressure to double what it was before. If it were possible to get α^2 , they would require to combine two volumes together by a process unknown to chemists, keeping the pressure and temperature as before. There was, in this respect, no doubt, an idea which differed from the mere collocation of symbols. The unit of ponderable matter described in the system was one which had been derived by chemists from chemical considerations alone. It had also been advocated by physicists from considerations derived from the theory of heat. In order to decide with certainty on the truth or falsehood of the atomic theory, it would be necessary to consider it from a dynamical point of view. He meant that kind of dynamics treated of in books on mechanics. It was worth while to direct the attention of chemists to the fact that a belief in atoms conducted necessarily to exactly the same definition as was given there—namely, that for every kind of substance the number of atoms, or molecules, in the gaseous state, occupying the space of a litre, at a temperature of 0 degrees, and of a pressure of 760 millimetres, must necessarily be the same. That was a consequence which could be deduced from purely dynamical considerations on the supposition advocated by Professor Clausius and others, that gases consist of molecules floating about in all directions, and producing pressure by their impact. That theory was now under probation among chemists, physicists, and others. The next step was one which might be far off—the finding of the number of these molecules. That number was a fixed one; and when it could be arrived at, we should have another unit of ponderable matter—that of a fixed molecule.

Professor STOKES (on being invited by the President to join in the discussion) said he had very little to add to what had been said; but referring to the way in which the symbols of some of the elements were arrived at, he might say they were based upon the known laws of combination by volume. The chief feature which struck him in the system of Sir Benjamin Brodie was, that it allowed them to express the composition of bodies by a method which took in all their existing knowledge, and did not assume anything besides. Of course the mode of expression was liable to change with an increase of knowledge; but taking their knowledge at a fixed point, such as it was at the present day, the method expressed everything that was known without superfluous hypotheses. The question of binoxide of nitrogen was a very important one; for if the known vapour density of that substance was to be admitted, it would seem to resign the question in favour of Laurent's system. On the other hand, if they agreed to pass over that anomaly for the present—and all chemists would admit that there was an apparent anomaly about it—then they were led to Sir Benjamin Brodie's system.

Mr. WANKLYN said the remarks of Professor Stokes had suggested what probably would occur to every one in the room—that the new method was a one-volume system. The well-known system of Gerhardt was a two-volume system.

Dr. ODLING: The pleasure with which I have heard Sir Benjamin Brodie's lecture is, I am afraid, almost counterbalanced by the shock which my feelings received on hearing from Dr. Frankland that he questioned the positive existence of atoms. If Dr. Frankland's opinion on that subject was what he has stated, he has grossly deceived the chemical public. (Laughter.) The Chairman has said quietly aside to me that, after all, Dr. Frankland never really believed in atoms, or he would not have ventured to take such liberties with them. We have been led to believe that not only have we atoms, but that these atoms

possess imaginary prongs, and that there is an imaginary clasping between them by means of these imaginary prongs, in a sort of hermaphroditism which it is scarcely possible to refer to. It behoves chemists to give their attention to this matter, as it affects their fundamental notions of chemical constitution and chemical change. After all, the system of symbols is a method of expression, and its value must depend upon its usefulness, upon the accuracy with which it expresses, and the facility with which it can be used. The accuracy with which Sir Benjamin's system can express, has been brought out in the part of his paper already published; but we wait for information on the facility with which the method can be used, and the advantages attending upon its use. It appears to me to possess one prominent merit, and that is expressed by the author in his paper—that the expressions are brought into immediate relations with the facts themselves. The present method of chemical expression, really, is not based directly upon the facts, but upon the facts through the intervention of the atomic theory. There is nothing of this kind in the method which the lecturer has introduced to the Society. No doubt the expression bears a relation directly to the fact, be the theory what it may. In the ordinary use of our present symbolic language, there are some chemists who, differing from Dr. Frankland, do believe in atoms, but who, not differing from Dr. Frankland, bring the idea of atoms prominently forward. On the other hand, there are some who, like myself, do not believe in atoms, and who keep the idea of atoms in the background as much as possible. But whether we do or do not believe in atoms, it still remains true that our notation is based upon the atomic theory, and without the atomic theory our language has no meaning whatever. One of the advantages of the new method is, that it is not inconsistent, by any means, with the atomic theory; but it is not based upon it. Another point of view from which the system commends itself even more strongly to our attention, is that which has been adverted to by Mr. Wanklyn, and which it does not require anybody to point out—namely, that it is a one-volume system, while the method which has been hitherto in use is a two-volume system. Laurent, however, has also introduced a one-volume system; but in that of the present author there is this additional feature: that it is the only mode introduced to chemists by which the volumes of substances can be represented by integral numbers without fractions. In Laurent's system there are fractions. It seems a thing altogether ridiculous that, under any system, we should adopt, as a unit of chemical substances, that which consists of two units, and which we are obliged to express in every way as consisting of two units. The new system is the first in which all prime factors can be written by an integral number. Another point of interest is the dissipation of that extraordinary law of even numbers which was brought into notice by Laurent and Gerhardt. Why that law should exist upon the atomic hypothesis, which is a dualistic hypothesis—the hypothesis which also exists in the expressions based on Laurent's one-volume system—is truly inconceivable; but in the mode of expression introduced by Sir Benjamin Brodie, this disappears altogether, and we get, at any rate, an entire series of compounds formed by the simple increment of atoms, one upon another, and without any of the objections which the ordinary formulæ present. Dr. Frankland has adduced, as a recommendation to this method, that it really introduces a great deal of hypothesis. There is no doubt that the whole system, as compared with the system of α^2 , is based upon an hypothesis; but with the exception of that hypothesis, I do not think that there is anything hypothetical in the whole system. Admit, for one instant, the not improbable hypothesis that the unit of weight of hydrogen is an indivisible quantity, and all the remaining portion follows as a matter of course. There remains only the question whether the consequences, which the adoption of

such an hypothesis leads to, are of such a character as to confirm the hypothesis, and, in fact, to demonstrate its truth. On that point I must say that I feel the difficulty which has been suggested by Dr. Frankland respecting the bodies which chemically behave in a different manner, and which are distributed in a different way, although, judging from their mere formulæ, it would be supposed that they should be distributed in an identical way. We have no means of separating, in our minds, that hydrogen which is distributable from that which is not. Altogether, I view the paper as of very great use to chemists, as calling upon them to consider the grounds upon which their present opinions are based, and as shattering to the ground a great many of the superstructures which have been raised upon the old theory. The paper is of the highest importance and the greatest interest. I feel, as many must have felt upon former occasions, that a blow has been given to one's long-cherished convictions. But, at the same time, I am not at the present moment inclined to abandon them altogether. I look upon myself as vanquished for the moment, but I am not altogether disinclined to renew the combat, when further knowledge shall give me the means of doing so.

Mr. BRAYLEY said that it appeared that one of the most striking and important elements of the subject which Sir Benjamin Brodie had placed before the Society, had not been adverted to by any of the gentlemen who had joined in the discussion. That was, the probability which it shadowed forth of discovering the compound nature of some of our present elements by a kind of chemical calculus. Professor Stokes had characterised the new method as embodying the representation of all we knew, but it appeared to add to this a hypothetical shadowing forth of what we might hope to know hereafter. It would be acceptable to chemists if the author would have the goodness to explain the manner in which he arrived, by his method, at the conclusion that whatever was represented by α (whether hydrogen or any other substance) was contained in all those haloid elements to which the sign of α was attached, such as chlorine, iodine, and bromine.

Mr. FOSTER said he thought the point which must strike chemists, at first sight at any rate, as the most interesting result of Sir Benjamin Brodie's method, was that it enabled them to arrive at the conclusion that some elements were, in point of fact, compounds. This, however, was by no means the first time it had occurred in the history of the science that chemists had arrived, by pure reasoning, at the conclusion that some substances, whose elements they did not know, were compounds. For instance, before it was known that the alkalies and the alkaline earths could be separated into oxygen and a metal, the majority of chemists were pretty well convinced that they were compound substances. And with regard to chlorine itself, that substance was, at its very discovery, viewed in a manner which was analogous to, if not, in point of fact, identical with, the view which was indicated by Sir Benjamin Brodie's notation. Hydrogen, hydrochloric acid, and chlorine were regarded in early times as bodies which formed a series with each other, hydrochloric acid being exactly half-way between hydrogen and chlorine. One point which had been alluded to, as well by Dr. Frankland as by Dr. Odling, was that the symbols exhibited in the diagram did not, in all cases, express quite as much, from some points of view, as the ordinary chemical formulæ. For instance, the formulæ of sulphuric acid and of nitric acid did not show that the sulphuric acid was what was commonly called bibasic, and nitric acid monobasic. That, he thought, was hardly a fair criticism upon the formulæ. For sulphuric acid the symbol was $\alpha\theta\zeta^2$; for nitric acid the symbol was $\alpha\eta\zeta^2$. But although the symbol representing hydrogen occurred merely once in each formula, still, having regard to the other letters, these tell us that the hydrogen is distributable in one case and not in the other. Take again the similar cases of water and hydrochloric

acid. The first was represented by $\alpha\xi$, and the other by $\alpha\chi$. One of the properties of the symbol χ was to render the α with which it was combined undistributable, whereas the ξ combined with the hydrogen rendered the hydrogen distributable; so that although α occurred once only in the formulæ of water and hydrochloric acid, the other letters showed that its properties varied. They should, therefore, judge of the formula, not by one of its signs alone, but by the varied meaning due to the collocation of symbols.

Dr. WILLIAMSON (Chairman): I cannot refrain from expressing on my own behalf, what I am sure must have been felt by all present—the strong sense of the obligation, under which we are placed to our eminent colleague, for the most laborious and most important work which he has been carrying on for many years, though it is only now becoming known to chemists. It is a peculiarly difficult thing to dissociate oneself from the prevailing ideas on such a subject as has been put before the Society; and yet such dissociation is essential to the working out of any truly new conception, and especially any new mode of expression. The novelties of expression which Professor Maxwell spoke of as having been a shock to him, are in themselves the essential condition of the working out of the new system of notation. One is, perhaps, pained on first hearing that 1 is equal to zero. Nor are we accustomed to understand an operation performed merely upon space. I must confess that although I have given considerable time and attention to the paper, I do not feel that I am in a condition to fully appreciate all the expressions used in that part of the system already published. There are some things which I feel hardly able to accept on the present basis; but, at the same time, I feel that until one can understand in plain English and in ordinary words the meaning of those operations and things denoted, it will be exceedingly presumptuous to doubt the correctness of results which have *prima facie* evidence of great consistency. Every chemist must be struck with the unity and consistency of the new method; but those qualities cannot be attributed to the present system of notation. I am quite convinced that whatever modifications Sir Benjamin Brodie's system may undergo at the hands of its author, its introduction will inaugurate an exceedingly important era in chemical language and notation. I am sure the Society will join with me in thanking the author most cordially for the great intellectual feat which he has performed in working out this subject, and in hoping that before long he may accomplish some further steps in his great work.

The Lecturer's Reply.

Sir BENJAMIN BRODIE: I do not know that there really remains very much for me to say upon this matter. With many of the remarks that have been made, both by Professor Frankland and by Dr. Odling, I cannot but agree. I think, myself, that the object of a method is not simply to give us statical formulæ, but that we must also consider the dynamics of the science. I mean, by "statical formulæ," that we are not merely to consider what matter is, but that we are to consider the laws also by which matter changes; and that is a point upon which I hope to throw some light at a future time, in the second part of the paper. It is then that the question will naturally arise as to the way in which the kind of facts, which it has been attempted to express by the theories of atomicity, will appear in this method. You must not suppose, because I have not entered upon these subjects, that I have ignored them; I only postpone the consideration of them. With regard to the other point, about the relative merits of this mode of statement and the one ordinarily in use, I think that some of the remarks of Dr. Frankland, and my friend Dr. Odling too, are based simply upon a misconception. Dr. Frankland seems to imagine, in the case of such symbols as those of nitric acid $\alpha\nu\xi^3$, and of sulphuric acid

$\alpha\theta\xi^4$, that the important and fundamental distinction which is assumed in our present system to consist in the different number of atoms of replaceable hydrogen which these substances respectively contain, is altogether obliterated and lost sight of. But this is not so. By simple inspection of the symbols, you can ascertain precisely, as in our present notation, the changes of this order of which chemical substances are susceptible. But, as Professor Foster justly observes, you must take into account the whole symbol, and not a bit of it only. If you take into account the fact that the matter of all known chemical substances is identical with the matter of the elementary bodies, then there is nothing to be added. To one who is familiarised with the use of these expressions (when this point is properly regarded), it is at once apparent that, whereas we can perform two of the operations, for example, symbolised in χ , and two only of those operations, upon the symbol $\alpha\theta\xi^4$, we can perform one, and one only, of those operations upon the symbol $\alpha\nu\xi^3$. These important questions, however, cannot be thus briefly discussed, and I must defer their consideration to other opportunities.

ORIGINAL COMMUNICATIONS.
ON SOME POINTS OF CHEMICAL PHI-
LOSOPHY.

BY
AUG. KEKULÉ,
Professor of Chemistry at the University of Ghent.

I. Introduction.

SCARCELY any chemist at the present day speaks of Radicals or of Types; and yet the type-theory, like its forerunner, the dualistic view, had its good points. It would, I think, be wise, not wholly to lose sight of these several theories, which, after all, are based upon a considerable number of facts.

All chemists, or at least the greater number of them, are at present adherents of the so-called *theory of atomicity*. Many declare their adherence to it without hesitation; others, for reasons peculiar to themselves, have hesitated to adopt the theory immediately, or at least to proclaim a decided adherence to it; nevertheless they have adopted some of its most important ideas, and have thus, unconsciously perhaps, become adherents of this theory, or at least are not far from becoming so.

Hence it might appear as if the time were at length arrived in which all chemists, or at least the majority of them, would be of one mind in respect to theory. But on closer examination we may easily convince ourselves that this is not the case, but rather that the views of the several adherents of the theory of atomicity exhibit very essential points of difference. For while some invent hypotheses with the view of obtaining the most satisfactory and consistent explanations of experimentally established facts, others develop the principles thus established to a greater extent, and thus construct a chemistry of formulæ which runs side by side with the chemistry of facts, as something to a certain extent independent of it. Others, again, though availing themselves of the same principles, keep to the form rather than to the idea, and seem to think that the chemical constitution of a body is explained as soon as it is represented by a formula constructed according to the principles now in vogue.

But it is not only in the application of principles that differences are found to exist; the views themselves, and even the fundamental ideas of atomicity entertained by different chemists, likewise exhibit wide diversity. Some regard atomicity as a fundamental property of matter, and therefore as fixed and unalterable, like the weight of the atoms, whereas others define it as the maximum of saturating capacity;

We need not comment upon the important memoir which commences in the next column. The name of its author will secure for it the attention it deserves, and it must be admitted that this subject is particularly interesting at the present moment. The latter sections will be illustrated with carefully executed engravings.

others again—and this last-mentioned view appears at present to have the greatest number of adherents—assume a varying atomicity, regarding the same element as monatomic, biatomic, triatomic, or even pentatomic, etc., according to circumstances. The most consistent have naturally gone so far as to divide all elements into two groups, exhibiting respectively odd and even atomicity, the elements of the first group having, according to circumstances, the atomicity 1, 3, 5, 7 ... n ; those of the second the atomicity 2, 4, 6 ... n .

We cannot say with certainty whether the theory of atomicity has gained in clearness and scientific value by these developments; but we must confess that to us the contrary appears to be the case, and that the contempt with which mathematicians and physicists regard the present direction of theoretical chemistry may, perhaps, be attributed to these lawless extensions of the atomic hypothesis.

As an adherent of the theory of atomicity, I feel myself under an obligation to consider a few disputed points relating to it from my own point of view. Perhaps I may succeed in bringing back this theory, which appears, in many instances, to have deviated from the right course, to a direction in which it may be of real use to science. I do not intend to develop my views in systematic order, or to submit the several questions to an exhaustive discussion, but shall rather allow individual, and often independent, considerations to follow one another in unconnected order; it will afterwards be easy to unite the results thus obtained into a systematic whole.

I must here also make a remark of a different kind. My object being merely to bring to light the greater or less probability of the theories under consideration, and not to write a history of the development of our theoretical views, I shall not, except in particular cases, give the names of authors, or the references to their memoirs, with regard either to the views which I attack, or to those which I defend.

II. *On the Existence of Chemical Atoms.*

The question whether atoms exist or not has but little significance in a chemical point of view: its discussion belongs rather to metaphysics. In chemistry we have only to decide whether the assumption of atoms is an hypothesis adapted to the explanation of chemical phenomena. More especially have we to consider the question, whether a further development of the atomic hypothesis promises to advance our knowledge of the mechanism of chemical phenomena.

I have no hesitation in saying that, from a philosophical point of view, I do not believe

in the actual existence of atoms, taking the word in its literal signification of indivisible particles of matter. I rather expect that we shall some day find, for what we now call atoms, a mathematico-mechanical explanation, which will render an account of atomic weight, of atomicity, and of numerous other properties of the so-called atoms. As a chemist, however, I regard the assumption of atoms, not only as advisable, but as absolutely necessary in chemistry. I will even go further, and declare my belief that *chemical atoms exist*, provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses. Should the progress of science lead to a theory of the constitution of chemical atoms—important as such a knowledge might be for the general philosophy of matter—it would make but little alteration in chemistry itself. The chemical atom will always remain the chemical unit; and for specially chemical considerations we may always start from the constitution of atoms, and avail ourselves of the simplified expression thus obtained, that is to say, of the atomic hypothesis. We may, in fact, adopt the view of Dumas and of Faraday, “that whether matter be atomic or not, thus much is certain, that, granting it to be atomic, it would appear as it now does.”

After these remarks, it is scarcely necessary to say that I set but small value on most of the attacks recently made against the atomic hypothesis. In many of them I see merely words and phrases, not ideas. It is, however, quite otherwise with the endeavours of those who seek to discover chemical laws independently of the atomic hypothesis. All endeavours of this kind possess great merit; and if they lead to actual results, the laws thus discovered independently of the atomic hypothesis, will be reducible to that hypothesis, and will follow as consequences from it, always supposing that the atomic hypothesis itself is true.

Brodie's ‘Calculus of Chemical Operations’ is an attempt of this kind. But the talented author of these speculations evidently goes too far, when he declares “that Dalton's theory is inadequate for present purposes, and that it could no longer be advantageously used to elucidate the work carried on by chemists;” and when he adds “that chemistry had got on the wrong tack—off the rails, in fact.”

A final verdict on these speculations cannot at present be pronounced, seeing that we have before us merely the method of drawing conclusions, and the application of this method to the construction of formulæ for the elements and for particular compounds. The author promises, indeed, that his method will present

numerous and important advantages, and he hopes, further, "to be able to express, by formulæ, dynamical facts;" but all these points are reserved for future communications. We may, however, even now assert that the published results, and especially the formulæ given for the elements and compounds, possess no advantage whatever over the views now universally received. They contain, like those hitherto in use, only statics, and no dynamics, and although we are assured "that they express, by symbols, the exact facts of chemistry," it is impossible not to perceive that these symbols involve an almost unlimited number of hypotheses for which there is no proof whatever.

For the elements, Brodie, as is well known, comes to the conclusion that there exist three groups, expressible by the symbols—

$$x \quad y^2 \quad x + y^2.$$

All elements belonging to the third group (chlorine, bromine, iodine, nitrogen, etc.) are regarded as compounds. They are not, indeed, supposed to contain two kinds of matter at present unknown in the separate state; but the much less admissible hypothesis is made that they consist of a constituent hitherto unknown in the isolated state, combined with *hydrogen*.

Such an assumption is so directly at variance, not only with all views hitherto received, but with the entire range of known facts, that it requires to be tested with all possible circumspection.

Even admitting at the outset that Brodie's speculation is founded "on a very fair amount of hypothesis," we cannot avoid seeing at the first glance that it leads to hypotheses of most astounding character, and on closer examination we are inevitably led to the conclusion that the entire speculation is based on pure caprice. Its foundation involves especially the three following hypotheses:

- (1) Hydrogen must be assumed as the starting-point.
- (2) Hydrogen is an element.
- (3) Hydrogen is the result of a single operation, therefore = α .

With regard to the first, it must, at all events, be admitted that, instead of hydrogen, any other element ought to be admissible as the starting-point of the system. But if chlorine (= x) or nitrogen (= y) had been selected for this purpose, no calculation could have led to the conclusion that these bodies contain hydrogen. Now, it is clear that a system of symbols cannot be admitted as a true representation of actual facts, unless its results are independent of the particular member of the system which has been taken as a starting-point for the construction of the whole.

The second hypothesis, that hydrogen is an element, might have been admitted without remark by every chemist who regards as elements all bodies not hitherto decomposed; but the author of the speculations now under consideration is under an obligation to show grounds for such an assumption, inasmuch as he comes to the conclusion that others of the so-called elements are compounds.

The third point, and perhaps the most important in connection with results, is no less hypothetical. Why is hydrogen regarded as the result of a single operation, and not as the result of two, seeing that oxygen, sulphur, etc., are supposed to result from two operations? We are assured, "There were strong reasons for preferring the use of the system in which α was employed to present the standard amount of matter;" but these reasons are not yet made known, and therefore their value cannot be appreciated. So much, however, is certain, that, if instead of α , the expression α^2 had been chosen for the purpose just mentioned, Brodie's own form of reasoning would have led to formulæ identical in every particular with those now in use. All bodies which we now regard as elements would, or, at least, might have been found to be such; and for all compounds, the system in question would have led to the very formulæ which have long been used by the adherents of the atomic molecular theory.

The hypothesis, hydrogen = α , is said to be the simplest that could be adopted; but it may be laid down as a general rule that, in selecting from a number of different hypotheses the one which is most probable on the ground of simplicity, it is necessary to look, not only to the relative simplicity of the hypothesis itself, but to the more or less simple character of the consequences which follow from it.

Had the author of the "Calculus of Chemical Operations" merely expressed an opinion that the formulæ which he has constructed for elements and compounds are "one of the different expressions" which, according to the principle of prime factors, are deducible from the known facts connected with relations of volume, everybody would have agreed with him. We should have perceived (though, perhaps, with some surprise) that our existing hypotheses are not the only ones capable of accounting for these relations of volume; and we should have been strengthened in the conviction that the correctness of our present theories and formulæ does not depend for its proof on volume-relations alone. But the author of this new mode of representation goes further. Among other things he plainly puts forward the view that many of the substances now re-

garded as elements contain hydrogen; and suggests that, even if the elements which are combined with hydrogen in these compounds do not exist in the free state on our earth, they may possibly exist in that state in other parts of the universe.

No one will maintain that the bodies which we now call elements are necessarily and absolutely undecomposable. But if, on the other hand, it be asserted that our existing elements are actually of compound nature, the establishment of such a proposition will certainly require more than the simple observation, that a result of the kind may possibly be deduced from a kind of reasoning founded upon hypothesis. We shall, at least, require proof that such an assumption is calculated to lead to useful results, and that it presents decided advantages over our present views. If it be maintained that many of the substances now regarded as elementary contain a substance at present unknown in the free state, combined with another body—hydrogen, for example—which we do not know in that state, we may, certainly, require the assertion to be proved by the actual separation of hydrogen from these substances. In default, however, of further knowledge, we may hold fast by the principle announced by Dalton, "that a substance, till it is decomposed, must be regarded, according to the just logic of chemistry, as an elementary substance."

When we consider the great services which the atomic theory has rendered to science, and the simple manner in which it explains and co-ordinates so large a number of chemical and physical phenomena we cannot but believe that a systematic development of this hypothesis will open out a wide prospect of advancement in our knowledge of chemical laws.

Such a development of the atomic hypothesis is, in fact, the introduction of what is now known as the *theory of atomicity*.

In its old form, as it has been admitted into chemistry since the time of Dalton, the atomic hypothesis has served to account for a variety of phenomena. It explained the constancy of chemical combining proportions, the law of multiples, etc.; and afterwards, when the ideas of atom and molecule were more sharply distinguished one from the other, an explanation was afforded of a new and by no means inconsiderable class of facts. But we were still quite unable to explain why the atoms of individual elements unite in the actually observed proportions, and not in others.

To explain this last-mentioned class of chemical phenomena, the theory of atomicity has been devised; and this theory—as indeed we

may already perceive—can be regarded as justified, and as possessing scientific value, only on the condition that it explains actually, or at least as far as possible, the facts for which it is intended to account.

The next communication will contain—

III. *On the Constancy of Atomicity.*

IV. *On Graphic and Glyptic Formulæ.*

LONDON WATER.

Bishopsgate Street Pump: Changes produced by keeping the Water. By E. T. CHAPMAN.

A SHORT time since, an examination of some London pump-water was published,* and amongst them was the water of a pump in Bishopsgate Street. I have made another examination of the same water, and have observed the changes which it undergoes on keeping. The water was collected July 4, and portions of it were examined at intervals. The first examination was made the same day.

The results were in milligrammes per litre, or parts in the 1,000,000:

Free Ammonia.†	Ammonia from Urea.	Ammonia from Albuminoid matter.
6.0	1.5	.25

After two days' keeping the free ammonia was slightly increased; after four days it was 7.0, and after six days it was 7.5; all the urea had therefore disappeared. After two days more the free ammonia had decreased to 7.0. At this time the water was still clear, and had no smell, though it had been exposed in a sunny place. On the tenth day the water was still clear; it was not again looked at till the fourteenth day, when it was found to be green and opaque, something like a solution of nickel which has been exposed to the air. It was examined on the fifteenth day (July 19). It would not filter, passing almost unaltered through filter-paper, or else stopping it up, so that one drop came through in five minutes. On adding potash, which occasions a precipitate in the freshly taken water, the whole of the green stuff was carried down by the precipitate as a green curd, and the water filtered at once quite clear. The unfiltered water was subjected to the same estimations to which it had been subjected on collection, with the following results:

Free Ammonia.	Ammonia from Urea.	Ammonia from Albuminoid matter.
1.64	0.00	7.18

The albuminoid matter had therefore in-

* See LAB., July 6, p. 252.

† In the table published of the results of the examinations of the pump-waters, etc., in this and some other cases, the ammonia from urea had not been determined, and was returned along with the free ammonia.

XXXI.—*On the Atomic Theory.*

By Prof. A. W. WILLIAMSON, Pres. Chem. Soc., F.R.S., &c.

THERE are considerable differences, not to say discrepancies, between the statements made by different chemists on the subject of the atomic theory. In some text books of the science the replacing values of so-called equivalent weights of elements are described as being the atomic weights of those elements, while in the same and in other books, statements are made respecting the principles of the determination of atomic weights which lead to different numbers from those representing the replacing values.

It sometimes happens that chemists of high authority refer publicly to the atomic theory as something which they would be glad to dispense with, and which they are rather ashamed of using. They seem to look upon it as something distinct from the general facts of chemistry, and something which the science would gain by throwing off entirely.

Thus, in one book we find the statement:—"It appears from this that 2×8 , or 16 parts of oxygen is the smallest quantity of oxygen that can be supposed to enter into the reaction just considered, if we would avoid speaking of fractions of equivalents; and we shall find hereafter that the same is true with regard to all other well defined reactions in which oxygen takes part. Hence, this quantity of oxygen, 16 parts by weight (hydrogen being the unit), is called an indivisible weight, or atomic weight, or one atom of oxygen."

And again:—

"The question whether matter is infinitely divisible, or whether its divisibility is limited, remains, at the present day, in the same state as when it first engaged the attention of the Greek philosophers, or perhaps that of the sages of Egypt and Hindostan long before them."

Another author says:—

"The law of multiple proportions being founded on experimental facts, stands as a fixed bulwark of the science, which must ever remain true; whereas the atomic theory by which

we now explain this great law may possibly, in time, give place to one more perfectly suited to the explanation of new facts."

When we refer to the author's enunciation of this great law, in a paragraph which is referred to as containing a statement of the law, we find it stated that in the compounds of oxygen and nitrogen the oxygen is in the proportion of 1, 2, 3, 4, 5 to one and the same quantity of nitrogen, and that no compounds exist containing any intermediate quantity of oxygen.

Another distinguished chemist also lays down that the atomic weight of each element is made to agree as far as possible with the three following conditions:—

1st. The smallest proportion by weight in which the element enters into, or is expelled from a chemical compound, the weight of hydrogen so entering or leaving a chemical compound being taken as unity.

2nd. The weight of the element in the solid condition, which, at any given temperature, contains the same amount of heat as seven parts by weight of lithium at the same temperature.

3rd. The weight of the element which, in the form of gas or vapour, occupies, under like conditions of temperature and pressure, the same volume is one part by weight of hydrogen.

Now, if we endeavour to determine according to these rules the atomic weight of phosphorus, we may compare the quantity of hydric chloride containing one part by weight of hydrogen with that weight of phosphoric chloride PCl_5 , which contains the same weight of chlorine, viz., $\frac{\text{P}}{5}\text{Cl}$. In this latter com-

pound, $\frac{\text{P}}{5}$ or 6.2 parts of phosphorus, has entered into combination with 35.5 parts by weight of chlorine, instead of one part by weight of hydrogen, which unites with 35.5 of chlorine in forming hydric chloride. 6.2 is, therefore, according to this rule, taken by itself, the atomic weight of phosphorus. We should not be justified in adopting the weight of phosphorus derived from an analysis of the lower chloride, PCl_3 , because the rule directs us to take the smallest proportion, and the proportion of phosphorus in PCl_5 is smaller than in PCl_3 .

If instead of the chloride we take the acid P_2O_5 , or a phosphate such as PO_4Na_3 , and compare them respectively with $5\text{H}_2\text{O}$ and $\text{H}_5\text{Na}_3\text{O}_4$, we obtain the same atomic weight for phosphorus, 6.2. By the second rule (if we interpret it as

meaning the capacity for heat between two given temperatures), we find that seven parts of lithium, if heated from 0°C. to 1°C. , absorb 6.59 degrees of heat, while one part by weight of solid phosphorus absorbs .1885. We have, consequently, the atomic weight 34.9, which, considering the nature of the determinations, may be accepted as a reasonable approach to the atomic weight 31, now adopted by chemists.

According to the third rule, we obtain for phosphorus the atomic weight 62, inasmuch as P^6 occupy in the state of vapour under like conditions the same volume as H^2 .

In the case of all elements, the first rule gives the smallest weight. Thus, calcium, in the calcic nitrate, $\text{Ca}(\text{NO}_3)_2$, replaces hydrogen in hydric nitrate in the proportion of 20 to 1. Oxygen in carbonic oxide replaces hydrogen by marsh-gas in the proportion of 4 to 1; in most of its compounds in the proportion of 8 to 1. Nitrogen in sal ammoniac replaces 5 atoms of hydrogen in the molecules 4HH and HCl , in the proportion of $2\frac{1}{2}$ to 1.

Another distinguished author describes—

- “The law of definite proportions;
- “The law of multiple proportions; and
- “The law of equivalent proportions.”

He subsequently describes the “hypothesis of the atomic constitution of matter,” the word hypothesis being no doubt intended to indicate an opinion on his part that the atomic constitution of matter is open to more doubt than the so-called law of multiple proportions, &c. Again, in another able book we find it stated that to each element is assigned a “particular number, termed its proportionate number, which expresses the least indivisible proportion of the element that is found to enter into a combination,” hydrogen being taken as the unit,—a very intelligible description of the atomic weight of the element. In illustration of these so-called proportional numbers, the author gives Gerhardt’s table of atomic weights, which were in use at the time his work was written. He avoids the word atom in describing his indivisible proportions, although later on he occasionally falls into the use of the common words “atomic weight,” and atom. When he comes to explain molecules and equivalents, there is no more talk about proportional numbers.

It certainly does seem strange that men accustomed to con-

sult nature by experiment so constantly as chemists do, should make use of a system of ideas of which such things can be said. I think I am not overstating the fact, when I say, that, on the one hand, all chemists use the atomic theory, and that, on the other hand, a considerable number of them view it with mistrust, some with positive dislike. If the theory really is as uncertain and unnecessary as they imagine it to be, let its defects be laid bare and examined. Let them be remedied if possible, or let the theory be rejected, and some other theory used in its stead, if its defects are really as irremediable and as grave as is implied by the sneers of its detractors.

But if the theory be a general expression of the best ascertained relations of matter in its chemical changes, the only general expression which those relations have as yet found, and be hypothetical only in so far as it presupposes among unknown substances relations analogous to those discovered among those which are known, then it must be classed among the best and most precious trophies which the human mind has earned, and its development must be fostered as one of the highest aims and objects of our science.

It cannot be desirable to leave the question on its present footing; and if we have any opportunity of bringing the existing doubts and misgivings to a distinct issue, it cannot be right to delay such a consummation.

Such are the feelings which induced me to accept the invitation with which the Council has honoured me, and to bring before you an analysis of the evidence of the present atomic theory, as I conceive it to exist dispersed in the minds and among the hands of chemists at the present time.

I propose to consider the subject under three successive headings.

1st. The proportions by weight in which elements replace one another, or their so-called equivalent weights, and the multiples of those proportions.

2nd. The units of chemical action, or the so-called molecules.

3rd. Atomic values.

Equivalent Weights.

Quantitative analyses have shown that the weight of oxygen which combines with one part by weight of hydrogen to form water, is eight times as great as that of the hydrogen; that the

weight of chlorine which combines with one part by weight of hydrogen to form hydric chloride is 35.5 times as great as that of the hydrogen. Whenever we displace oxygen from water by chlorine, forming hydric chloride, we find that for every eight parts by weight of oxygen so displaced, thirty-five and a half parts by weight of chlorine are taken up; and whenever we perform the opposite substitution, viz., displace chlorine from hydric chloride by oxygen so as to form water, we find the inverse ratio, viz., eight parts by weight of oxygen, replacing 35.5 parts by weight of chlorine. These numbers, 8 and 35.5, represent the relative weights in which oxygen and chlorine combine with the unit weight of hydrogen, and they are called the equivalent weights. The decomposition of ammonia by heat yields nitrogen gas and hydrogen in the proportion of $4\frac{2}{3}$ parts by weight of nitrogen to one of hydrogen, and in like manner the decomposition of marsh-gas yields three parts by weight of carbon to every one of hydrogen. Moreover, when we displace nitrogen from ammonia by chlorine, forming hydric chloride, we find that chlorine takes the place of the nitrogen in the proportion of 35.5 parts to $4\frac{2}{3}$; and in like manner when chlorine displaces carbon from marsh-gas forming hydric chloride, it does so in the proportion of 35.5 parts to 3 of carbon. So also when oxygen replaces carbon in marsh-gas forming water, we find that eight parts of oxygen take the place of three of carbon.

We have accordingly, from the comparison of these hydrogen compounds,—

35.5	as the equivalent weight of chlorine,		
8	“	“	oxygen,
$4\frac{2}{3}$	“	“	nitrogen,
3	“	“	carbon.

But chlorine can be made to replace the hydrogen in marsh-gas by successive steps, and we find that it does so in the proportion of 35.5 parts by weight to one part of hydrogen, and in the product so formed hydrogen can be made to replace chlorine, reproducing marsh-gas always in the proportion of one part by weight to 35.5 of chlorine.

Upon this and similar evidence we attribute to hydrogen, in relation to chlorine, the equivalent weight 35.5, and by so doing we extend our meaning of the word equivalent. 35.5 parts of chlorine are equivalent to 8 of oxygen, because they combine

with the unit weight of hydrogen; and 35.5 of chlorine are equivalent to one of hydrogen, because the elements replace one another in that proportion by weight in their compounds. In like manner oxygen can be made to replace hydrogen in ammonia and in marsh-gas, forming nitrous acid and carbonic acid respectively. It there reacts in the proportion of the same equivalent weight which it has in relation to chlorine. Nitrogen and carbon can, partly by such-like direct reactions, and partly by indirect reactions, be proved to replace hydrogen in the proportion of the same weights in which they combine with it. So that the equivalent weights of chlorine, oxygen, nitrogen, and carbon are the weights of those elements capable of combining (directly or indirectly) with the unit weight of hydrogen, or of replacing the unit weight of hydrogen.

Several other metals have been found to be analogous to hydrogen, viz., lithium, sodium, potassium, silver, &c., and to replace it in combination with chlorine or oxygen in the proportions corresponding to the following equivalent weights:—Lithium 7, sodium 23, potassium 39, silver 108, &c.; and in like manner bromine and iodine have been found analogous to chlorine, and to replace it in equivalent weights corresponding to 80 of bromine and 127 of iodine.

In the compounds ClH , ClK , BrH , BrK , ClAg , ICl , BrLi , OH_2 , OHK , ONa_2 , OClH , NH_3 , NH_2K , NK_3 , CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CO_2 , the elements are contained in proportions corresponding to the equivalent weights above mentioned. But there are other compounds in which they occur in different proportions; thus iodine combines with chlorine in the proportion of 127 to 35.5, and also in the proportion of $42\frac{1}{2}$ to 35.5; nitrogen also combines with hydrogen and chlorine in the common compound, sal-ammoniac, and in the other compounds like it, in the proportion of $2\frac{1}{2}$ to every one of hydrogen or the equivalent weight of another element. Carbon combines with oxygen in a second proportion in carbonic oxide, viz., that of 3 to 4, and with hydrogen in many other proportions besides that which occurs in marsh-gas: viz., in methyl, four parts of carbon to one of hydrogen, in olefiant gas, six parts of carbon to one of hydrogen, and in acetylene, twelve parts of carbon to one of hydrogen, besides many others intermediate between these.

Now, Dalton knew the two oxygen-compounds of carbon, besides marsh-gas and olefiant gas. He represented the oxide

as containing one equivalent of oxygen weighing 8, with one of carbon weighing 6; the acid as containing twice 8 parts by weight of oxygen, combined with 6 of carbon.

In like manner, he considered olefiant gas as a compound of one equivalent of carbon, weighing 6, with the unit of hydrogen, marsh-gas as 6 of carbon with two units of hydrogen.

Some other compounds he found, partly by his own analyses, partly by analyses made by other chemists, to contain their elements in proportions approaching to simple multiples of certain weights peculiar to those elements respectively. He explained this coincidence by representing compounds as built up of atoms of their elements in various proportions to one another.

Many other elements are now known to combine in various proportions, which may be so represented, and it is common to refer to the fact which Dalton explained by atoms, as the law of multiple proportions.

It is desirable that we analyse the evidence which is now before chemists of these multiple proportions, and further their connection with the atomic theory.

The analyses known to Dalton have by the progress of chemistry been, for the most part, replaced by others more accurate and more trustworthy, and some of the numbers representing the combining proportions of elements, have undergone considerable modifications in consequence of our improved methods of observation; but both Dalton and we agree in one respect, viz., that taking the best numbers we can get by analyses, we calculate the composition of every compound, on the assumption that it must be built up of integral multiples of certain numbers belonging to the elements respectively; and it must be admitted as a *primâ facie* confirmation of the justice of this assumption, that the more perfect our methods of observation become, and the more carefully they are applied, the more nearly do our experimental results agree with multiple proportions of such numbers.

In the case of compounds of very simple constitution, the agreement between our experimental results and the theory of multiple proportions is so close, that it would be unreasonable to attribute the coincidences to chance. But, on the other hand, the progress of research leads frequently to the discovery of compounds of which the constituents are present in less simple

proportions, and others again in which the proportion can be represented only by high numbers. And in many cases the difference between the numbers corresponding to the formula which is admitted, and the numbers corresponding to some other formula, is not greater than the unavoidable errors of experiment. So that analysis does not decide which of the formulæ is the true one, nor does it furnish an argument in favour of any formula. Thus a high term of the marsh-gas series, such as $C_{27}H_{56}$, cannot be analysed with certainty. The numbers found by combustion were—

C 85.5

H 14.9.

The formula $C_{27}H_{56}$	the formula $C_{26}H_{54}$	and	$C_{27}H_{54}$
requires C 85.27	requires C 85.25	requires	C 85.71
H 14.73,	H 14.75,		H 14.29

The actual result of observation agrees with none of these formulæ, yet, in examining it, chemists assume that it ought to agree with some such formula. They select the most probable, and attribute to errors of observation the divergence from it.

The most important evidence brought to bear on the composition of this body was of two kinds: first, an examination of a silver-salt, formed from the product of its cautious oxidation, and containing the following percentages, viz. :—

C 62.36

H 10.31

Ag 20.92,

which approach more nearly to the numbers—

C 62.66

H 10.25

Ag 20.9,

required by the formula $C_{27}H_{53}AgO_2$, than to any other probable formula; and, secondly, a study of the action of bromine upon it proving that it was a marsh-gas and not an olefiant gas, like that last mentioned.

The hydrocarbon itself approached nearer in composition to the formula $C_{27}H_{56}$ than to any other, and the study of two of its reactions thus agrees in indicating that formula for the original hydrocarbon as more probable than any other atomic formula.

It would be quite correct to say that *some* elements are found capable of uniting with one another in the proportion of simple multiples of certain weights, and not in intermediate proportions. Thus carbon unites with oxygen in the proportion of 12 parts of carbon to 16 of oxygen, and also in the proportion of 12 of carbon to 2×16 of oxygen. If we take less oxygen than 16 parts to every 12 of carbon, some of the carbon remains as such uncombined, and no compound of the two elements has ever been got with less oxygen than 16 parts to every 12 of carbon. But if we take more and more oxygen in proportion, we find that carbon can unite with it till it has got 2×16 parts. Yet we do not admit that it unites in all proportions intermediate between 16 and 2×16 , for by examining these products, formed by adding more and more oxygen to the compounds of 16 grammes with 12 carbon, we find that they are mixtures of carbonic acid and carbonic oxide; the former being rapidly soluble in aqueous potash, whereas the latter remains undissolved.

But the theory of multiple proportions is not limited in so modest a manner. It is applied to all elements and to all compounds of them, in spite of the fact that the usual results of observation require straining to agree with any multiple formula, and the immense majority of substances have not as yet been reduced by the process to any definite formulæ whatever. The very great majority of mineral and of organic substances which we meet with on the surface of the earth, have not been proved to have a composition agreeing with any formula.

When multiple proportions are spoken of, it is not usually explained whether multiples of equivalent weights are meant, or multiples of the atomic weights of the elements. It is sometimes asserted that we have a law of multiple proportions, which is a direct representation of experimental facts, whereas the atomic theory is a hypothesis, and independent of such law. Those who make this statement must be understood to refer to multiples of equivalent weights, and not to multiples of atomic weights; for if, as they assert, atomic weights are hypothetical, then any relation between the multiples of atomic weights are only multiples of hypothetical numbers, and cannot have greater certainty than the atomic weights themselves.

If we knew the empirical proportions of elements, and did

not believe in atoms, we should describe carbonic oxide as the compound of three parts of carbon with four of oxygen, and carbonic acid as the compound of three parts, by weight, of carbon with eight of oxygen. The hydrocarbons mentioned would be described as follows, viz.: marsh-gas, as a compound of three parts of carbon with one of hydrogen; olefiant gas, a compound of six parts of carbon with one of hydrogen; methyl, a compound of four parts of carbon with one of hydrogen; ethyl, a compound of twenty-four parts of carbon with five of hydrogen; and so on. We should probably use the simplest entire numbers corresponding to the actual proportion between the elements; but we should not use the higher numbers standing to one another in the same proportions which are introduced by the atomic theory.

It is quite true that the elements of some simple, well-known compounds are shown by analysis to be present in proportions corresponding to simple multiples of a particular weight belonging to each of them respectively; but in compounds of less simple constitution, no such relation is obvious. The analysis of most organic bodies does not suggest any simple proportion between the numbers of those weights of their constituents, and it sometimes suggests a relation which is not the true one. Thus, the only simple representation of the results of analyses of the high term of the marsh-gas series above mentioned, would be to describe it as containing six parts, by weight, of carbon to one of hydrogen. The actual process by which we establish the composition of such complex bodies is by *assuming* that the composition of each of them must correspond to entire multiples of the atomic weights of their elements, and by treating as errors of observation any divergence between the proportions discovered by analysis and such atomic proportions.

It is not easy to judge of the evidence of one part of a system by itself. The doctrines of equivalence, of molecular weights, and of atoms mutually support one another, and are habitually used by chemists in connection with one another. Our present task is to examine the doctrine of multiple proportions of equivalents; first, in respect of the evidence upon which it rests; secondly, in respect of the proof which it affords, if any, of the existence of atoms.

The second question may be best investigated in the form of a comparison between the atomic method of multiples, and

what I may be permitted to call the tomic method of sub-multiples; carbonic acid is represented in the atomic plan as containing twice as much oxygen as is contained in carbonic oxide; whereas, on the other plan, it may be represented as differing from carbonic oxide by containing half as much carbon as is contained in the oxide. It is true that by combining oxygen with carbonic oxide we get carbonic acid; but it is equally true that by combining carbon with carbonic acid we obtain carbonic oxide. As far as the proportion of the elements is concerned, we have no better right to suppose that the carbon is indivisible, and that the acid contains twice as much oxygen as the oxide, than we have to suppose that the carbon is divisible, and that half of the carbon is taken out of carbonic oxide in forming carbonic acid.

We cannot be too careful in considering this fact, for many important consequences follow from it. Our proposition relates to an undefined quantity of carbonic oxide. It is known that by combining four parts, by weight, of oxygen with seven parts by weight of carbonic oxide, we get exactly eleven parts of carbonic acid; or, what is the same thing from another point of view, that if we take away four parts of oxygen from eleven of carbonic acid, we get seven of carbonic oxide. It is also known that if we take away 1.5 parts of carbon from 7 of carbonic oxide, we get 5.5 parts of carbonic acid; and, reciprocally, that if we add 1.5 parts of carbon to 5.5 of carbonic acid, we get 7 of carbonic oxide. These parts by weight may be tons, or pounds, or ounces, or grains, or any other actual experimental weight. A philosopher disbelieving in the existence of atoms, would point out that whereas the divisibility of matter is infinite, we find that by the chemical processes available for the removal of carbon from carbonic oxide, the carbon divides into equal portions, one remaining with the oxygen, the other leaving it; and his statement that this half of the carbon is added on again when the process is reversed, is as consistent with the evidence as that of the believer in atoms, who asserts that in forming carbonic acid, oxygen is added in quantity equal to the oxygen in the carbonic oxide, while the formation of carbonic oxide from the acid consists in taking away half the oxygen. What has been here said of the proportions between the elements in carbonic oxide and carbonic acid may be said with equal force

of the proportions between the elements contained in other compounds, such as the following :—

$\text{FeCl}_2, \text{FeCl}_3, \text{CH}_4, \text{CH}_3, \text{CH}_2, \text{C}_2\text{H}_3, \text{CH}, \text{NH}_3, \text{NH}_4\text{Cl}, \text{SH}_2, \text{SCl},$
 $\text{OH}_2, \text{OH}, \text{PI}_2, \text{PCl}_3, \text{PCl}_5, \text{ICl}, \text{ICl}_3, \text{SiCl}_4, \text{SiF}_6\text{K}_2, \text{PtCl}_2,$
 $\text{PtCl}_4, \text{PtCl}_6\text{K}_2, \text{BF}_3, \text{BF}_4\text{K}, \text{AuCl}, \text{AuCl}_3, \text{AuCl}_4\text{Na}, \text{CrCl}_3, \text{CrCl}_3,$
 $\text{CrF}_6, \text{SnCl}_2, \text{SnCl}_4, \text{HgCl}, \text{HgCl}_2, \text{CuI}, \text{CuCl}_2.$

If we examine consistently with the principles above adopted, the equivalent weight of each element contained in these compounds, we find that we must describe it as the weight which in any compound is combined with the unit of hydrogen, or might be replaced by it. This is easily obtained by dividing the number represented by the atomic symbol by the number of equivalents of the hydrogen or chlorine families with which it is combined.

We thus obtain the values :

$\frac{\text{Fe}}{2}, \frac{\text{Fe}}{3}, \frac{\text{C}}{4}, \frac{\text{C}}{3}, \frac{\text{C}}{2}, \frac{2\text{C}}{3}, \frac{\text{C}}{3}, \frac{\text{N}}{3}, \frac{\text{N}}{5}, \frac{\text{S}}{2}, \frac{\text{S}}{2}, \frac{\text{O}}{2}, \frac{\text{O}}{2}, \frac{\text{P}}{2}, \frac{\text{P}}{3}, \frac{\text{P}}{5}, \frac{\text{I}}{3}, \frac{\text{I}}{4}, \frac{\text{Si}}{4},$
 $\frac{\text{Si}}{8}, \frac{\text{Pt}}{2}, \frac{\text{Pt}}{4}, \frac{\text{Pt}}{8}, \frac{\text{B}}{3}, \frac{\text{B}}{5}, \frac{\text{Au}}{3}, \frac{\text{Au}}{5}, \frac{\text{Au}}{2}, \frac{\text{Cr}}{3}, \frac{\text{Cr}}{6}, \frac{\text{Cr}}{2}, \frac{\text{Sn}}{2}, \frac{\text{Sn}}{4}, \text{Hg},$
 $\frac{\text{Hg}}{2}, \text{Cu}, \frac{\text{Cu}}{2}.$

I have taken only a few of the well known compounds, yet among them there are ten elements, each of which has two distinct equivalent weights, four of the elements have got three equivalent weights each, and another (carbon) is shown to have five different equivalent weights. It might easily be shown to have many more.

Now it is interesting to observe that whenever examples are given of the supposed law of multiple proportions, Chemists take not these fractional expressions representing equivalents, but usually the atomic symbols themselves. They describe, in fact, *atoms* as occurring thus combined with one another in the proportions of entire multiples of their weight; in fact, the so-called law of multiple proportions has no existence apart from the atomic theory; those who adopt it seem not to be aware that they are using the notion of atoms, or else they are shy of mentioning it.

The fact that two elements, such as carbon and oxygen, are

capable of combining in more than one proportion is in reality (when we consider it by itself) quite as much an argument against the atomic theory as an argument in favour of it. That the carbon in carbonic oxide can be divided in the proportion of $\frac{1}{3}$, or the oxygen can be multiplied in the proportion of 2 to 1, are equally true statements of the proportion. If oxygen could neither take more nor less carbon than in the proportion of three parts by weight to every four of oxygen, we could say with certainty that that proportional weight of carbon cannot be divided, or in other words that it is an atomic proportion; but the existence of the two compounds, although not inconsistent with the atomic theory, points as much to proportional divisibility of carbon as to proportional multiplicability of oxygen.

When one of those who profess to disbelieve in the atomic theory has ascertained by analysis the percentage composition of a compound, and wants to find its formula, he divides the percentage weight of each element by its atomic weight. He seeks for the smallest integral numbers which represent the proportion of atoms, and he attributes to impurity of his sample or to errors of analysis any deviation from the atomic formula thus obtained. He looks to the reactions of the body for aid in constructing his atomic formula, and controls his analyses by considerations derived from well established reactions, but whenever he is led by any of these considerations to a formula which contains a fraction of any atomic weight, he takes a multiple of the formula sufficiently high to be entirely free from such fractions. In no case does he reason on a basis independent of the atomic theory.

Existence of Molecules.

The atomic theory led to the discovery of molecules. Chemists saw in the phenomena of combination in multiple proportions, processes which were in accordance with their pre-conceived belief in atoms, and they studied combining proportions from the point of view of atoms. They acted on the assumption that each element consists of small indivisible particles of like nature; that the atoms of each element are different in many chemical properties, and usually in weight, from those of every other element; that the unlike atoms combine

together in various relative numbers to form clusters, or so-called molecules, every pure compound consisting of such molecules, each one like the rest, but differing from the molecules of every other compound. Thus a given quantity of carbonic oxide was supposed to consist of an aggregate of molecules, each one composed of an atom of carbon united with an atom of oxygen; carbonic acid, to consist of molecules, each one built up of three atoms, viz., one of carbon, and two of oxygen. In calculating the molecular weight of any compound from the ascertained proportion of its elements, they assumed that each molecule must contain at least such a number of atoms of each of its elements as would, when multiplied by the atomic weight of the respective elements, represent the actual proportion by weight in which the elements had combined. Thus 44 parts by weight of carbonic acid have been found to contain 32 of oxygen, and twelve of carbon. Two atoms of oxygen, each weighing 16, with one atom of carbon weighing 12, must be contained in the smallest existing particle of carbonic acid.

Ammonia contains hydrogen and nitrogen in the proportion of 3 parts of the former to 14 of the latter. 3 atoms of hydrogen, each weighing 1, with one atom of nitrogen weighing 14, represent the simplest molecular constitution corresponding to that proportion of the elements. The molecule of olefiant gas, in like manner, must contain at least one atom of carbon with two atoms of hydrogen, while that of marsh gas contains at least one of carbon with four of hydrogen.

An acid hydric salt, the tartrate, was found by analysis to contain carbon, hydrogen, and oxygen, in proportions corresponding to the minimum formula $C_2H_3O_3$. When neutralised by potash, its solution yielded a potash salt corresponding to the minimum formula $KC_2H_2O_3$, and it is known that the weight of hydric sulphate indicated by the formula $\frac{SO_4H_2}{2}$ or $\frac{S}{2}O_2H$ would react on the same weight of potash forming a neutral salt. This relation between the tartrate and sulphate may be expressed by saying that 75 parts by weight of the tartrate are equivalent to 49 parts by weight of the sulphate.

In like manner a compound of basic properties, called quinia, was found to contain carbon, hydrogen, nitrogen, and oxygen, in proportions which can be represented by the minimum formula $C_{10}H_{12}NO$. It was found that the base unites with hydric

chloride, and forms a platinum-salt, analogous to the salt formed by ammonia, and known to have the composition $\text{PtCl}_6\text{H}_2(\text{NH}_3)_2$. The weights of these bases denoted by the formulæ NH_3 and $\text{C}_{10}\text{H}_{12}\text{NO}$, are accordingly equivalent to one another in the sense in which we have hitherto used that word. It is well known that, in the actual development of our knowledge of these relations, the notion of equivalence sprang up among acids and bases, and was extended from them to elementary bodies.

It is interesting and instructive to observe that, for a considerable time, the proportions in which compounds react on one another were represented by formulæ according to the atomic theory as it then prevailed, which recorded the empirical proportions of the constituents, but were not correct or consistent representations of the molecular weights. These labours served to collect an immense amount of evidence for the establishment of molecular weights, but the end was not distinctly in view, and the only rational guide was the imperfect atomic theory then existing.

Thus the great Berzelius, the master spirit of that period, used formulæ which in our system of atomic weights may be thus rendered:

Water	H_2O
Potash	K_2O
Potassic hydrate	$\text{H}_2\text{OK}_2\text{O}$
Nitric acid.....	N_2O_5
Potassic nitrate	$\text{K}_2\text{ON}_2\text{O}_5$
Hydro-potassic sulphate	$\text{H}_2\text{OSO}_3\text{K}_2\text{OSO}_3$
Ether.....	$\text{C}_4\text{H}_{10}\text{O}$
Alcohol	$\text{C}_4\text{H}_{10}\text{OH}_2\text{O}$
Carbonic acid	CO_2
Carbonic chloride.....	CCl_4
Phosgene	CO_2CCl_4
Chloro-sulphuric acid	$2\text{SO}_3 + \text{SCl}_6$
Chloro-chromic acid.....	$2\text{CrO}_3 + \text{CrCl}_6$
Bismuthic oxychloride.....	$\text{Br}_2\text{O}_3\text{BrCl}_3$
Hydric chlor-acetate ($\text{C}_2\text{Cl}_3\text{HO}_2$)..	$\text{C}_2\text{O}_3\text{C}_2\text{Cl}_6\text{H}_2\text{O}$
Hydric oxamate ($\text{C}_2\text{NH}_3\text{O}_3$)	$\text{C}_2\text{O}_3\text{H}_2\text{OC}_2\text{O}_2\text{N}_2\text{H}_4$
Bichlorinated ether ($\text{C}_2\text{H}_3\text{Cl}_2$) ₂ O..	$2\text{C}_4\text{H}_6\text{Cl}_6\text{C}_4\text{H}_6\text{O}_3$.

Some of his atomic weights were inconsistent with our mole-

cular formulæ. Thus hydrogen, chlorine, nitrogen, and some other elements, he really treated as having atomic weights twice as great in relation to oxygen as we now consider them to have. For his couple of volumes of hydrogen, denoted by the symbol H , were not allowed to separate from one another, so that his formula HO for water was in its uses similar to the formula HO , and analogous to his formula for potash, which was written KO .

The theory of radicals did much towards classifying compounds. The names ammonium and cyanogen were given to groups of elements which exhibited analogies with single elements. Ethyl was another radical which did admirable service; and benzoyl afforded an instance of a radical of another kind.

The theory of organic radicals is in reality an extension of the atomic theory, and it was needed as a step towards the proof of that theory.

The equivalent proportions of elements, and the multiples of those proportions in which they combine, afforded no proof of the existence of atoms, but they led to the discovery of compound atoms analogous to undecomposed atoms. At the same time, many of these organic radicals, although exhibiting the closest analogy with elements, are known to be only capable of existing under certain conditions, and are easily burnt or decomposed.

It was a great step to extend the use of the word atom to groups of elements known to hold together only under certain limited conditions. For by including in one common term, atom, the smallest particles of the elements, and the smallest particles of these compounds which behave like elements, we deprive the word atom of the only objectionable peculiarity of which it might have been accused. It is no longer an absolute term; and in its application to the elements it denotes the fact that they do not undergo decomposition under any conditions known to us. If anybody use the word in its absolute sense in its present applications, he is guilty of a manifest inconsistency.

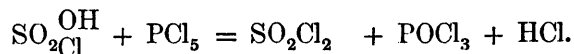
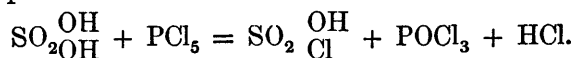
It must not, however, be supposed that the existence of groups of elements, which perform functions analogous to those of single elements, is any proof of the existence of atoms, for compounds like $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_{16}\text{H}_{33}\text{Cl}$, NH_4Cl , $\text{C}_6\text{H}_7\text{Cl}$, &c., may be

represented as containing submultiples of the less numerous atoms, just as NH_3 can be represented as $\frac{\text{N}}{3}\text{H}$, or CO_2 as $\frac{\text{C}}{2}\text{O}$.

One of the most fruitful ideas in the work of establishing the molecular constitution of compounds, was the idea of types—and the correlative idea of substitution. If we maintain unity of type, the knowledge of a few molecular formulæ serves as a guide to many others. Thus, if we take water as H_2O , alcohol can be proved by normal substitutions to be $\text{C}_2\text{H}_6\text{O}$. We find that phosgene reacts upon alcohol according to the equation $\text{C}_2\text{H}_5\text{OH} + \text{COCl}_2 = \text{C}_2\text{H}_5\text{OCOCl} + \text{HCl}$, whereas, if the molecular formula of Berzelius for phosgene were true, the first action would be $\text{C}_2\text{H}_6\text{O} + \text{C}_2\text{O}_2\text{Cl}_4 = \text{C}_2\text{H}_5\text{OC}_2\text{O}_2\text{Cl}_3 + \text{HCl}$; the second action would be the formation of the compound $\text{C}_2\text{O}_2\text{Cl}_2\text{O}_2(\text{C}_2\text{H}_5)_2$.

The process is a mere replacement of chlorine by $\text{C}_2\text{H}_5\text{O}$, forming a compound of the molecular formula $\text{C}_3\text{H}_5\text{ClO}_2$, instead of one of double that formula. Now, having found that as small a weight as COCl_2 can take part in one distinct reaction, we know that the molecular weight is not greater than that. Again, the molecular formula of water being known, we have the reaction $\text{SO}_2\text{Cl}_2 + \text{H}_2\text{O} = \text{SO}_3\text{HCl} + \text{HCl}$, and $\text{SO}_3\text{HCl} + \text{H}_2\text{O} = \text{SO}_4\text{H}_2 + \text{HCl}$, which establish for chlorosulphuric acid the maximum formula SO_2Cl_2 , and for hydric sulphate the formula SO_4H_2 . So also the hydric chloracetate reacts on a molecule of potassic hydrate thus, $\text{C}_2\text{HCl}_3\text{O}_2 + \text{HOK} = \text{C}_2\text{KCl}_3\text{O}_2 + \text{H}_2\text{O}$. In these reactions there are alternative explanations: thus, if phosgene is $\text{C}_2\text{O}_2\text{Cl}_4$, then the ether $\text{C}_3\text{H}_5\text{ClO}_2$ must have double that molecular weight: for the reaction is a regular double decomposition, in which no indication of increase or diminution in the number of molecules takes place.

With the chloro-sulphuric acid there is a similar alternative. $\text{S}_3\text{O}_{12}\text{H}_6$ must be the molecular formula of hydric sulphate, if $\text{S}_3\text{O}_6\text{Cl}_6$ be that of the chloro-acid: for the above reaction is as normal as possible, and, moreover, we can recover the chloro-acid from the hydric salt by a couple of steps as normal, as far as the sulphate is concerned:—



In order to judge of the evidence of molecular weights obtained by a study of chemical reactions, we ought to consider, on the one hand, what properties must belong to compounds built up of atoms, and, on the other hand, what properties might belong to them if there were no limit to the divisibility of each kind of elementary matter.

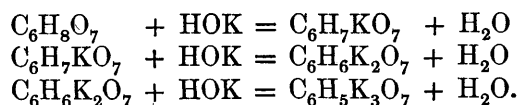
Now the first and most essential characteristic of every molecule is that it possesses a weight equal at least to the sum of the atomic weights of its constituents, in such number as represents the simplest proportion consistent with a correct analysis. Thus a compound containing iron and oxygen in such proportions by weight as correspond to three atoms of oxygen to every two atoms of iron, must have at least as great a molecular weight as $2 \times 55 + 3 \times 16$. On the other hand, if iron and oxygen, when combined in this proportion, were infinitely divisible, one would be able to get smaller weights of the oxide to take part in reactions, than such as are 160 times as heavy as the unit weight of hydrogen. We can replace the oxygen in this oxide by chlorine; we can combine it more or less fully with sulphuric acid, or with other acids; we can decompose these salts by other compounds; we can combine them with other salts; and we can compare each of these products with the original oxide, quantifying the proportions of the materials which take part in each transformation: and the result of it all is that we get a chain of evidence proving that less than 160 parts of ferric oxide never take part in any reaction.

So again with other bodies.

Thus a base composed of carbon, hydrogen, and nitrogen was obtained, which could not be represented by a simpler formula than $C_6H_{15}N$. The atomic theory tells us that less than $72 + 15 + 14 = 101$ parts by weight of this base cannot possibly take part in any reaction. We bring it in contact with hydric chloride in varying proportions, beginning with very little of the chloride. By examining the product, we find it is a mixture of the unchanged base with a compound containing carbon, hydrogen, nitrogen, and chlorine, in proportions corresponding to the formula $C_6H_{16}NCl$, and containing exactly 101 parts of the base with one part by weight of additional hydrogen and 35.5 parts of chlorine. If we add our hydric chloride to the base, exactly in this proportion, we have nothing left of either material uncombined with the other; and if we add more hydric

chloride, such excess is left uncombined and unchanged. The base does react on hydric chloride in the proportions indicated by its atomic formula, and has not been found to react in any other proportion.

Take an acid salt like hydric citrate, $C_6H_8O_7$, being the simplest atomic formula representing its composition. By bringing it in various proportions in contact with a solution of potassic hydrate, we find that it is capable of reacting in three distinct proportions on that basic hydrate—



If we look through the reactions of well-known bodies with one another, we find that there are many which are not made out quantitatively; but not one of the enormous number that we know accurately and with certainty, has shown a combining proportion of molecules at variance with the atomic theory, and corresponding to the idea that matter is infinitely divisible.

The density of gases and vapours has afforded valuable independent confirmation of the truth of the atomic constitution of molecules, for every compound which evaporates without decomposition has a vapour-density proportional to its molecular weight.

The great benefits conferred upon our science by the doctrine of types would have been impossible without the doctrine of radicals. The two theories were for a considerable time held by different chemists, and were supposed to be inconsistent with one another. They have proved to be essential to one another; so that it may confidently be asserted that those who showed that NH_4 may replace an atom of hydrogen, of potassium, &c., and that C_2H_5 may also perform such functions, prepared the way for the comparisons of bodies of one type.

Another class of considerations which have done admirable work in establishing molecular weights, are those relating to the number of products of substitution obtainable by altering the proportion of materials.

Thus hydric sulphate not only forms the neutral potassic sulphate which we considered in relation to the neutral tartrate,

but it also forms a double salt containing hydrogen and potassium, according to the formula HKSO_4 , when it is brought in contact with half or less than half as much potassic hydrate as is needed to form the neutral salt; and the fact that the hydrogen in the sulphate can be replaced by potassium, in the proportion of half or all, gives an independent proof that the minimum formula of the hydric salt must be H_2SO_4 . So also the hydric tartrate forms, not only the neutral salt above mentioned, but also an acid double salt of hydrogen and potassium, for which the simplest formula is $\text{C}_4\text{H}_5\text{KO}_6$, and a double salt with sodium and potassium $\text{C}_4\text{H}_4\text{NaKO}_6$.

The common phosphates were proved by such evidence as this to be tribasic, and the oxalates, in like manner, to be bibasic. Other reactions confirm the conclusions thus arrived at. For instance, the bibasic salts yield two classes of amides—normal amides, such as oxamide $\text{C}_2\text{O}_2\text{N}_2\text{H}_4$, and compounds of amide and salt, like potassic oxamate $\text{C}_2\text{O}_2\text{NH}_2\text{OK}^2$; and monobasic salts are distinguished from these not only by their inability to react in more than one proportion on potash or soda, but also by their inability to form compounds of amide and salt, like the oxamate. Again, bibasic hydrogen salts lose their water by heat, and monobasic hydrogen salts do not.

The classification of compounds by their analogies has been one of the most important operations for enabling us to see their distinctive resemblances and differences, and the establishment of series of homologous organic compounds has been, perhaps, the most perfect and useful case of such classification, as well as one of the most fruitful of benefit to the progress of science.

So well did the analogies and reactions among organic compounds serve to connect them with one another, by simple and natural principles, that the simpler part of the science has gained chiefly of late years by adopting methods and conclusions established in the more varied field of organic compounds. Thus, the chief arguments adduced by Gerhardt for the molecular weight of carbonic acid which we now adopt, and for the corresponding molecular weight of water, were to the effect that in no reaction between well known molecules is a smaller proportion of carbonic acid given off or taken up than that corresponding to the molecular weight 44; and, in like manner, less

than 18 parts, by weight, of water are never taken up nor given off in any well known reaction between molecules of known weight. The examples of molecules in each case were mainly taken from organic chemistry. The molecular weights of the gaseous elements, hydrogen, chlorine, nitrogen, oxygen, &c., were studied in great part with the aid of the light obtained from the comparison of organic reactions, in which they take part, especially the double decompositions which take place when chlorine normally replaces hydrogen.

A study of the phenomena of electrolysis, and some other inorganic processes, had led to metals being considered as possessing, in the free state, a molecular constitution analogous to that of compounds; and Brodie's reduction of oxides by oxygen gave evidence of combinations between atoms of oxygen in forming the free gas.

Amongst the general processes which were instrumental in judging of the correctness of molecular formulæ was Gerhardt's so-called law of even numbers. Among molecular formulæ which he considered well established, he observed that the sum of the atoms of a certain list which he supplied was always an even number; whereas, the sum of the atoms of elements not belonging to his list was sometimes an even, sometimes an uneven number.

The circumstance is now known to be one among several consequences of a difference in replacing value, which constitutes one of the most important characteristics of atoms, and we also know that many elements which Gerhardt classed with hydrogen, nitrogen, &c., do not belong to that class; but even in its original imperfect form the rule rendered very important services. Thus, such formulæ as $C_2H_3O_3$, $C_{10}H_{12}NO$, Gerhardt knew could not be molecular formulæ, and must be at least doubled. A study of their reactions amply confirms his verdict. We also know that such formulæ as $FeCl_3$, $HgCl$, $AlCl_3$, cannot represent molecules, and must be corrected so as to contain at least even numbers of chlorine atoms without including the metallic atoms in the account.

To do justice to the completeness of the evidence which is obtained respecting many molecular weights, by these purely chemical methods of research, it would be necessary to go into the full particulars of the operations and observations in the respective cases, and that would task, still more unduly than I

am now tasking it, the indulgence of the Society. But I feel convinced that the brief indications which I am able to give of the kind of evidence obtained under these various headings, will recall to the minds of chemists the particulars which it would be needful to describe specially to persons not intimately acquainted with the science.

There are, however, other properties of molecules which have been noticed since chemists discovered the existence of the molecules themselves, and these are of kinds to be more easily understood by all—properties which involve no change of composition in the molecules, but which belong to them as long as they subsist.

Of these physical properties, one of the most important is the volume of molecules in the state of gas or vapour. Whenever we examine perfect vapours composed of like molecules, we find that whatever the molecules may be, they occupy the same volume under like conditions. In other words, these little units of matter, found by the guiding aid of the atomic theory, are found also to be units of force when examined under those conditions. There have, in several cases, been important discrepancies between the chemical evidence of molecular constitution and the evidence afforded by vapour-volume. Thus, hydric sulphate and ammoniac chloride are among the compounds of whose molecular weights we have the best and most varied chemical evidence, yet the vapour formed from each of these occupies about double the volume of a gas molecule. A careful examination of the vapour formed from each of them showed, however, that it is a mixture of molecules of two sorts formed by the decomposition of the original compound. The fact that errors in the indications supplied by vapour-density could be thus pointed out by the chemical evidence of molecular weight is surely no slight confirmation of the perfection of the evidence of molecular weights obtainable by chemical methods; and, on the other hand, the immense number of coincidences between the indications obtained from the two independent sources is a strong evidence of the truth and parallelism of the two.

There are, also, crystalline compounds, which chemistry has found to be closely analogous, which occupy, in the crystalline state, equal, or nearly equal, volumes.

Among other physical properties which confirm the truth of

the atomic views of molecular constitution are boiling points. Whenever truly analogous elements are comparable in respect to boiling points, it is found that those composed of heavier atoms boil at higher temperatures than those composed of lighter atoms. A comparison of the successive terms of the series—chlorine, bromine, and iodine, illustrates this difference very strikingly. So also a comparison of the several terms of the series—oxygen, sulphur, selenium, and tellurium, and not less so the elements nitrogen, phosphorus, arsenic, antimony, and bismuth.

Now, whenever volatile organic compounds belonging to a homologous series are compared, it is found that of two such compounds, the one having the higher molecular weight has also the higher boiling point. The glycols present, however, an exception to this general observation.

The melting points of homologous organic compounds also show differences running parallel in like manner to their differences of molecular weight.

The relative velocities of motion of particles, as shown by the processes of diffusion, afford another confirmation of the general truth of the molecular weights; for, on the one hand, it is known that heavy particles diffuse more slowly than light particles; on the other hand, a comparison of the relative velocities of movement of molecules of relative weights, previously determined upon chemical evidence, shows that the heavier molecule of chemistry is also the heavier molecule in diffusion.

At this point of my study of this question I am in a serious difficulty, for molecules have no *locus standi* in the absence of the atomic theory. They are, to use the words of Dumas, physical atoms; their existence is a necessary consequence of the atomic theory, and all chemical reactions agree in proving their existence. They are also discovered by an examination of the mechanical properties of gases.

The opponents of the atomic theory are bound to explain, in some other way, the facts which point so distinctly to the existence of molecules, if they wish to advance from the position of mere contradictors to that of chemists.

Hitherto they have not done so, and the case stands thus: on the one hand, we have a simple theory which explains in a consistent manner the most general results of accurate observation in chemistry, and is daily being extended and

consolidated by the discovery of new facts which range themselves naturally under it. On the other hand, we have a mere negation: for the statements of those who say that our evidence of the existence of atoms is not conclusive, and yet omit to show any alternative theory, are nothing more. In discussing the relative composition of carbonic acid and carbonic oxide, I have endeavoured to put the negation in a tangible form, as an affirmation that there are no limits to the divisibility of elements, and to represent compounds containing multiples of equivalent weights as containing sub-multiples corresponding to the same empirical proportions.

If elements, in combining with one another, merely undergo more minute subdivision, so that a compound, like amylic alcohol, $\text{CH}_{1\frac{1}{2}}\text{O}_{\frac{1}{2}}$, is formed from methylic alcohol by removing hydrogen and oxygen from the compound CH_4O , then we could expect a weight of it corresponding to a formula containing less hydrogen and oxygen to perform the functions of the molecule CH_4O .

Of two things, one: either the existence of molecules is denied, or it is admitted.

In the former case, the vast and consistent body of chemical evidence of the existence of molecules must be set aside and disproved, and the physical confirmations of their existence must also be proved to be erroneous.

In the latter case it must be shown by quantitative analysis that those complex molecules to which we attribute a great weight, are really lighter than their simpler analogues.

Now, the difficulty is to choose arguments for an opponent. It would probably matter little to us which they might select; but when they content themselves with saying that we are wrong, without either showing in what respect our evidence or our reasonings are at fault, and without showing any other evidence or any other reasonings which they consider preferable, it is difficult to know what else to do with them than to state our case and leave them to their reflections.

Atomic Values.

The most important and weighty chemical property of atoms as yet discovered, is one which can only be perceived by the aid of a knowledge of the equivalent weights of the elements and of the molecular weight of a considerable number of compounds.

Thus if we know the molecular formulæ of the following compounds, we can compare them with one another and perceive their differences of composition :

Hydric acetate has the molecular formula	$C_2H_4O_2$
Hydric monochloracetate	$C_2H_3ClO_2$
„ dichloracetate	$C_2H_2Cl_2O_2$
„ trichloracetate	$C_2HCl_3O_2$
Again,	
Marsh-gas has the molecular formula....	CH_4
Methylic chloride	CH_3Cl
Methylenic chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Carbonic chloride	CCl_4

It is apparent from these series of formulæ that one equivalent weight of chlorine can take the place of one of hydrogen in a molecule, or two of chlorine can replace two of hydrogen, or three replace three, and so on. Hydrogen-compounds containing in each molecule a much greater number of hydrogen equivalents, have been found to allow, in like manner, the hydrogen to be replaced, one equivalent at a time, by chlorine, and to the extent of a great number of equivalents in each molecule.

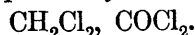
In like manner, potassium replaces hydrogen in molecules, sometimes in the proportion of an even number of equivalents, sometimes in the proportion of an uneven number of equivalents, as will be seen by the following molecular formulæ:—

H_2O	H_2SO_4	H_3PO_4	H_3N	$H_2C_4H_4O_6$
HKO	$HKSO_4$	H_2KPO_4	KH_2N	$HKC_4H_4O_6$
K_2O	K_2SO_4	HK_2PO_4		$K_2C_4H_4O_6$
		K_3PO_4		

When, however, oxygen takes the place of hydrogen, without change of equivalent weight, it is only in the proportion of two equivalents of oxygen replacing two of hydrogen, four of oxygen replacing four of hydrogen, six replacing six, and so on; always an even number of hydrogen equivalents replaced in each reaction of the kind. Thus carbonic acid is formed from marsh gas by the normal reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$, in which four equivalent weights of oxygen replace four of hydrogen. Hydric nitrate has a constitution similar to ammoniac hydrate, the difference being that it contains four equivalent

weights of oxygen instead of four equivalent weights of hydrogen in the ammonia, as will be easily seen by a comparison of the formulæ HONH_4 and HONO_2 .

Again, phosgene is methylenic chloride in which two equivalents of hydrogen are replaced by two of oxygen—



The compounds .. ammonia	$2\text{H}_3\text{N}$
nitrous acid.....	O_3N_2
glycoll.....	$\text{C}_2\text{H}_6\text{O}_2$
hydric glycollate	$\text{C}_2\text{H}_4\text{O}_3$
hydric oxalate.....	$\text{C}_2\text{H}_2\text{O}_4$

show a replacement of hydrogen by oxygen in steps, each one being two hydrogen replaced by two of oxygen. Now, it is not the existence of these compounds which proves any different value in oxygen atoms from chlorine atoms; it is the fact that no case is known of a molecule containing a single equivalent of oxygen in place of one of hydrogen, nor of three equivalents of oxygen in place of three of hydrogen, nor, in short, of any uneven number of hydrogen equivalents replaced by an uneven number of oxygen equivalents.

The same difference between oxygen and chlorine may be seen by comparing all well known molecular formulæ containing either one of those elements, apart from the particular process by which they may have been formed. Thus we have, by way of illustration, some bodies taken at random from various classes of compounds—

$\text{C}_2\text{H}_5\text{Cl}$	H_2O
$\text{C}_2\text{H}_4\text{Cl}_2$	CO
$\text{C}_2\text{H}_3\text{Cl}_3$	CO_2
$\text{C}_2\text{H}_6\text{ClN}$	$\text{C}_2\text{H}_2\text{O}_4$
$\text{C}_2\text{H}_5\text{Cl}_2\text{N}$	$\text{C}_2\text{H}_6\text{O}$
PCl_3	$\text{C}_5\text{H}_{12}\text{O}$
NH_4Cl	$\text{C}_4\text{H}_6\text{O}_4$
CrO_2Cl_2	$\text{C}_3\text{H}_8\text{O}_3$
SO_2Cl_2	$\text{C}_2\text{H}_3\text{OCl}$
SO_4H_2	$\text{C}_2\text{H}_4\text{OCl}_2$
PO_4HNa_2	
PbO_2H_2	
PbO	
PbO_2	

There are, however, some cases which at first sight do not agree with this general conclusion. Thus, on comparing potassic chloride with potassic oxide, it might be said that the equivalent weight of potassium in the former is combined with an equivalent weight of chlorine, and in the latter with an equivalent weight of oxygen; thus KCl , $\text{KO}_\frac{1}{2}$. But the answer is that this comparison is made in defiance of the known molecular formula of potash (K_2O), established by reactions and analogies which leave no doubt of its correctness. Whenever oxygen replaces chlorine in such a chloride, it binds together two basic equivalents, one from one molecule of the chloride one from another; and in like manner when chlorine replaces oxygen in any molecule, such as water H_2O or potassic hydrate, it loosens into two molecules what the oxygen held bound up in one. Thus, by passing oxygen and hydric chloride through a red-hot tube, we have a replacement of chlorine by oxygen, taking place, as far as it goes, according to the molecular equation $\text{O}_2 + 4\text{HCl} = 2\text{H}_2\text{O} + 2\text{Cl}_2$, half as many molecules of water being formed as molecules of hydric chloride are decomposed; and on the other hand if we send chlorine and steam through a hot tube, we break up a part of the steam, forming two molecules of chloride from every one of oxide.

When we apply the word atom to two equivalent weights of oxygen, and say that an atom of oxygen has a replacing value equal to that of two atoms of chlorine or of hydrogen, we give to a couple of equivalent weights of oxygen the name atom, as a record of the fact that we have never known them to divide, and that we must in all our considerations respecting oxygen bear in mind this peculiarity of it. In carbonic oxide it may be argued that an atom of oxygen takes the place of four equivalents of hydrogen of marsh-gas, and that it has there the equivalent weight 4, instead of its usual equivalent weight 8. But on the other hand the gas may be represented as containing carbon with an equivalent weight of double its usual one, viz., 6 instead of 3. In any case, the gas affords an instance of a change of atomic value, and if we describe the value of the atom of oxygen in disregard of this case, it is because we have to record its commonest value.

What has been here said of oxygen applies to sulphur equally. No molecule has ever been found containing an uneven number of equivalent weights of sulphur, and the atom of sulphur has

certainly the value of two chlorine or hydrogen. There are, however, strong reasons for believing that in some of its compounds its atom has a replacing value of four or even six. Selenium and tellurium are so closely allied to oxygen and sulphur in their reactions that their atoms are always classed together. In like manner bromine and iodine go with chlorine, and lithium, sodium, &c., go with hydrogen and potassium. Silver also has an atom of uneven value.

Nitrogen is found upon similar evidence to divide in no smaller proportion than that of three times $4\frac{1}{2}$, or 14 parts by weight, for whenever it has an equivalent weight of $2\frac{1}{2}$, as in NH_4Cl , its atom has five values.

It seems to me of paramount importance to the due understanding of the functions of this element, to state in the most direct and matter of fact way possible, the actual proportion in which its atom replaces hydrogen. If the replacing value of an atom be measured by the number of hydrogen atoms needed to replace it, then nitrogen has in ammonia the atomic value three, for three atoms of hydrogen are needed in order to replace one of nitrogen in NH_3 , forming three molecules of hydrogen H_3H_3 ; and in sal ammoniac it has just as distinctly the atomic value five, for five atoms of hydrogen are needed in order to take the place of one of nitrogen, forming one molecule of hydric chloride and four molecules of hydrogen: ClNH_4 becomes $\text{ClH} + \overline{\text{H}_4\text{H}_4}$. Sal-ammoniac is as well known a molecule as ammonia itself; each of them undergoes decomposition at high temperatures, the complex molecule not requiring so high a temperature for its decomposition as the simpler one. Those chemists who represent sal-ammoniac as containing one atom of nitrogen of the same value as in ammonia, seem to me to incur the disadvantage of stating rather what, according to their own theoretical notions *ought* to be, than what actually *is*, and thereby to lose sight of one of the most important of all properties of atoms, viz., the property of changing value under particular chemical and physical conditions which it is our business to study and describe.

I shall return to this important point somewhat later, and endeavour to trace an outline of the conditions of these changes.

Together with nitrogen are always classed the elements phos-

phorus, arsenic, antimony, and bismuth. Their atoms have frequently the value of three, but frequently also that of five. Boron has in its chloride and fluoride the value three, but in its double fluoride the value five— BCl_3 , BF_3 , KBF_4 . Gold is not proved to have any smaller atomic value than three, for we have no evidence of the molecular weight of the compound AuCl . Compounds corresponding to AuCl_3 and NaAuCl_4 , are common and tolerably well known.

Carbon is at present perhaps that element of which the compounds are best investigated. A comparison of the composition of an immense number of carbon-compounds has not led to the discovery of a single molecule containing a number of its equivalent weights, other than such as can be divided by four. Its atom is accordingly considered to weigh 12, and to have the value 4. In carbonic oxide, the atom of carbon has a somewhat uncertain value, according as we consider oxygen to vary in value or not. Silicium, titanium, and tin are in many respects so closely allied to carbon that it is to be expected that their atomic weight must be such as to give the atoms the value 4 in their ordinary compounds. The atom tin in stannous chloride appears at first sight to be worth 2, but the molecular formula of the compound is not known, and may possibly be Sn_2Cl_4 like olefiant gas. Silicium in its double fluoride, SiF_6K_2 , is evidently worth 8, and titanium and tin have also doubtless a higher value than 4 in their double salts.

Platinum seems to vary from four values to eight, as in the compounds PtCl_4 and PtCl_6K_2 . Its lower chloride PtCl_2 ought probably to have a higher molecular formula.

Not only does the empirical comparison of the number of equivalent weights of each element contained in well-known molecules lead to a discovery of the relative weights of atoms, but there are other chemical evidences which concur with these. Thus the univalent alkali-metals have long been known to be unable to form basic salts, whereas many multivalent metals form such salts with peculiar facility; witness antimony and bismuth, mercury and lead, in the compounds SbOCl , $\text{Bi}_2\text{O}_2\text{SO}_4$, $\text{Pb}(\text{HO})(\text{NO}_3)$. In such compounds as these, the metal performs the function of binding together several radicals or simple atoms, just as in water or potassic hydrate the oxygen binds the two atoms together; and when such a metal is removed, and an equivalent quantity of a single-

value metal supplied in its place, the atoms which had been bound together pass off, each in combination with its own atom of metal. Thus, in the reaction $\text{Pb} \begin{smallmatrix} \text{HO} \\ \text{NO}_3 \end{smallmatrix} + \text{Ag}_2\text{SO}_4 = \text{PbSO}_4 + \text{AgOH} + \text{AgNO}_3$ we have a severance of AgOH from AgNO, which would not take place if silver were of double its atomic weight, and, like lead, of the atomic value 2.

Double amides, such as $\text{Hg} \begin{smallmatrix} \text{Cl} \\ \text{NH}_2 \end{smallmatrix}$, and double salts, such as $\text{Ba} \begin{smallmatrix} \text{NO}_2 \\ \text{C}_2\text{H}_3\text{O}_2 \end{smallmatrix}$, $\text{Cu} \begin{smallmatrix} \text{AsO}_2 \\ \text{C}_2\text{H}_3\text{O}_2 \end{smallmatrix}$ are also evidences of the biacid character of the base, just as $\text{KNaC}_4\text{H}_4\text{O}_6$ is an evidence of the bibasic character of the acid.

Again, compounds of metals with organic radicals have furnished admirable evidences of the atomic weights of various metals whose equivalent weights are known. Thus the compounds $\text{Zn}(\text{C}_2\text{H}_5)_2$, $\text{Zn} \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{I} \end{smallmatrix}$, $\text{Hg}(\text{C}_2\text{H}_4)_2$, $\text{Hg} \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{I} \end{smallmatrix}$, $\text{Sn}(\text{C}_2\text{H}_5)_4$, $\text{Sn} \begin{smallmatrix} (\text{C}_2\text{H}_5)_3 \\ \text{Cl} \end{smallmatrix}$, $\text{Sn} \begin{smallmatrix} (\text{C}_2\text{H}_5)_2 \\ \text{Cl}_2 \end{smallmatrix}$, $\text{Pb}(\text{C}_2\text{H}_5)_4$, $\text{Pb} \begin{smallmatrix} (\text{C}_2\text{H}_5)_3 \\ \text{Cl} \end{smallmatrix}$, &c., have been among the best chemical evidences of the atomic values of the respective metals.

Similar proofs of the value of the atom of silicium have been given by the formation of molecules containing atoms of ethyl and chlorine together numbering *four*, just as in the molecule of marsh-gas the hydrogen can be replaced by chlorine in four distinct proportions.

Atomic Heat.

Perhaps the most direct confirmation of the atomic weights established upon evidence of the various kinds which we have been considering is afforded by the capacity for heat of elementary bodies. A comparison of the relative capacity for heat of solid elements showed that all atoms have nearly the same capacity for heat. Thus 23 grammes of sodium absorb, when heated from 0° C. to 1° C., almost exactly the same quantity of heat as 39 grammes of potassium when heated from 0° C. to 1° C.; and 210 grammes of bismuth absorb that same quantity when heated from 0° C. to 1° C. Silicium, carbon, and boron form exceptions to this law, but in all other cases the approximation

to equality between the numbers found for the several solid elements is admitted to be as close as can be expected from determinations involving so many difficulties, and including so many sources of error.

Like every other confirmation of the atomic theory, the law of atomic heat has contributed to the development and systematisation of that theory. It is well known that a considerable number of metals, such as lead, mercury, iron, tin, barium, &c., appeared, according to the atomic weights originally assigned to them, to have about half the atomic heat of the metals before mentioned, and that this circumstance was urged by an illustrious Italian chemist as an argument for doubling their atomic weights, so as to bring them within the law. It is also too well known to need illustration to you, that the chemical properties of those metals amply confirm the truth of Cannizzaro's proposition, that their atomic weights are twice as great as was formerly supposed. Indeed so much chemical evidence has now been accumulated, that we should certainly retain the higher atomic weights for lead, tin, iron, barium, &c., even if we knew nothing of atomic heat.

Atomic values are not so variable as equivalent weights. A most important light has been thrown on the phenomena of equivalence by our knowledge of atomic values and the general principle of their changes. The foundation of this consideration was laid by those chemists who proved that the molecule of chlorine consists of two atoms of chlorine combined with one another, and that the molecule of oxygen consists of two atoms of oxygen combined with one another.

It is well known that free carbon at high temperatures unites with hydrogen, forming acetylene, which has the molecular formula C^2H_2 . I will write the number belonging to each atomic symbol above, as an exponent, when I wish to represent the atoms so numbered as combined with one another, O^2 , &c., meaning a compound of an atom of oxygen with an atom of oxygen; C^2 a compound of an atom of carbon with another atom of carbon. On the other hand, I will write the number belonging to any atomic symbol below, when I wish to represent the atoms as not combined with one another. Thus H_2 means two atoms of hydrogen, and OH_2 means a compound of one atom of oxygen with two atoms of hydrogen, each of

which atoms of hydrogen is merely united with the atom of oxygen. It is merely an abbreviated form of writing HOH or

$\begin{array}{c} \text{HO} & \text{H} \\ | & | \\ \text{H} & \text{O} & \text{H} \end{array}$
 or O &c. By adding two atoms of hydrogen to acetylene

we get olefiant gas, C^2H_4 , and this again, in its turn, can be transformed into methyl C^2H_6 . These bodies, C^2H_2 , C^2H_4 , C^2H_6 , are well known to have molecular weights corresponding to two atoms of carbon in each, and the hydrogen is held in each molecule by being combined with the carbon. With more hydrogen the double atom of carbon cannot combine, for the next hydrocarbon to methyl is marsh-gas CH_4 containing a single atom of carbon.

Again, if we remove hydrogen from marsh-gas in the smallest possible proportion, we find that the atom of carbon in one molecule combines with one atom of carbon in another molecule, while they are losing their hydrogen. Methylic iodide reacts on zinc-iodomethide by a normal interchange of iodine for methyl $\text{H}_3\text{CI} + \text{IZnCH}_3 = \text{H}_3\text{CCH}_3 + \text{ZnI}_2$. It is admitted that the explanation of the molecular weight of methyl lies in the fact that it contains two atoms of carbon combined with one another to the extent of one-quarter of their value, and that this combination of carbon with carbon is the essential condition for the formation of such a complex molecule. But, if this be true, the other terms of the series are explained by a mere extension of the same principle. Ethylene contains two atoms of carbon H_2CCH_2 , each combined with two atoms of hydrogen, and each one combined with the other to the extent of two of its values. Acetylene, HCCH , is in like manner a compound of two atoms of carbon, each one combined with the other to the extent of three values.

It was known that an atom of carbon may combine partly with hydrogen, partly with some other element or elements, and it was also known that like atoms combine with one another; so that it was quite consistent with known facts to suppose that an atom of carbon may combine partly with another atom of carbon, partly with some other element. The simplification introduced into the chemistry of the compounds of carbon by this theory is, however, truly admirable, and, by itself, entitles the distinguished author of the idea to the high rank among theorists which he holds.

Carbon in all its compounds may have the same atomic value consistently with our present knowledge of those compounds. In carbonic oxide alone we are compelled to represent it as having only the value two, unless we attribute to oxygen the value four.

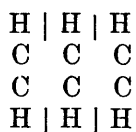
Among the instances of increase of equivalent weight in elements, there are a great number in which the element exhibiting that increase, by giving up some of the unlike with which it was united, unites with the like while doing so.

Thus, SCl_2 , by the mere action of heat, decomposes with evolution of chlorine, and by an atom of sulphur combining with another atom of sulphur, $2\text{SCl}_2 = \text{S}_2\text{Cl}_2 + \text{Cl}_2$. Water and hydric peroxide are doubtless related to one another, in the same manner, each of the two atoms of oxygen in the molecule of the peroxide being half combined with oxygen, half with hydrogen. Mercuric chloride loses half its chlorine, forming calomel, while the mercury unites to the extent of half its value with mercury, and cupric chloride is reduced to cuprous chloride by a similar process. On the other hand, phosphoric chloride loses chlorine, and forms phosphorous chloride, without any combination of phosphorus with phosphorus taking place. The equation $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ represents the process; and until it can be shown that the molecule of phosphorous chloride is a multiple of PCl_3 , the reaction must be accepted as direct evidence of a change in the atomic value of phosphorus from 5 to 3. In like manner, if ammonia be admitted to have the molecular formula NH_3 , the decomposition of sal-ammoniac by heat, according to the equation $\text{ClNH}_4 = \text{NH}_3 + \text{HCl}$, must be admitted as evidence of a change of atomic value in nitrogen from 5 to 3. When auric chloride is decomposed, with evolution of chlorine and formation of aurous chloride, the interpretation of the reaction requires evidence which we do not possess respecting the molecular weight of the lower chloride. If aurous chloride has the molecular formula AuCl , its formation is accompanied by a change of atomic value in the gold; but if its molecule contains more than one atom of gold, the metal may exist in both compounds with the same atomic value.

Among complex organic molecules there is, of course, considerable room for variety in the arrangement of atoms, which we may consider consistently with the empirical equivalent weight of the carbon.

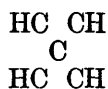
The hydrocarbon benzole is of so much interest from its derivatives, that it has attracted a good deal of attention, and to explain its molecular constitution, the six atoms of carbon have been represented as arranged in a ring, each atom being combined with the atom of carbon at one side of it to the extent of two values, and with the atom of carbon on the other side of it to the extent of one value.

Another arrangement, which was mentioned a good many years ago at this Society, is to consider each atom of carbon combined with three others, and with one atom of hydrogen. Such an arrangement is easily represented in space. Let the accompanying formula represent as unfolded in one plane, the group which would be formed by the carbon atom at one end of each line moving back through the paper until equidistant from the two others in the line.



I put bars between symbols of elements, which, for convenience, are juxtaposed, but which I do not wish to represent as combined with one another.

Naphthalin may, in like manner, be represented by the formula C^5H_4 , as containing four atoms of carbon, each united with two of the others and with one atom of hydrogen, while the fifth atom of carbon is combined with each of the first four.



With respect to the conditions under which changes of atomic value take place, some valuable information may be gained by comparing molecules known to exist in different states. Let any chemist write for himself a list of molecules known to exist in the liquid state alone, and not volatile without decomposition. Let him compare with that, a list of molecules known to evaporate unchanged; and thirdly, let him look at the molecular formulæ of the hitherto uncondensed gases. He will notice that in passing from the non-volatile to the uncondensed, he goes from complex molecules to simpler and

simpler ones. Let him compare the formulæ of products formed by destructive distillation with those of the materials from which they are formed. The examples may be taken from mineral and from organic chemistry. He will find some cases of the formation of a more complex molecule by distillation; but for one such he will find an enormous number of cases of the breaking up of complex molecules into more and more simple ones. Take, for instance, the series CO_3H_2 , SO_3H_2 , NH_5O , SbCl_5 , PCl_5 , SO_4H_2 , PO_4H_3 , $\text{C}_2\text{O}_4\text{H}_2$, NH_3 , CH_4 , H_2O , CO_2 , beginning with compounds so exceedingly unstable, that, working at ordinary temperatures, we hardly know them; and finishing by compounds of great stability, which are only broken up into simpler molecules at the most intensely high temperatures. The fact stares us in the face, that simple molecules correspond to high temperatures, complex molecules correspond to low temperatures. Several of these changes of composition are certainly accompanied by changes of atomic value. Whenever there is a change of atomic value effected by change of temperature, the lower atomic value corresponds to the higher temperature. These phenomena have attracted some attention of late, in consequence of Deville's researches on dissociation. I will give an example of the application of this principle to the study of reactions in illustration of the importance of seeing and recording differences of atomic value in elements.

I will again use the notation which I referred to above. The following formulæ give samples of nitrogen-compounds in which nitrogen has the atomic value 5: ClNH_4 , HONH_4 , $\text{HON}(\text{C}^2\text{H}_5)_4$, $(\text{H}_4\text{NO})_2\text{CO}$, $(\text{H}_4\text{NO})_2\text{C}^2\text{O}_2$, H_4NOCCH_3 . The action of heat

upon them gives rise to NH_3 in two cases, $\text{N}(\text{C}^2\text{H}_5)_3$, $(\text{H}_2\text{N})_2\text{CO}$, $(\text{H}_2\text{N})_2\text{C}^2\text{O}_2$, H_2NCCH_3 . In each case the nitrogen-atom is

reduced to the value of 3. In fact it will be seen that in ammonium-salts nitrogen is worth 5, in amides only worth 3. Ammonia is an amide in this sense.

Among chemical evidences of atoms, the discovery of the distinction between direct and indirect combination is worth consideration, more especially as it is independent of the quantitative comparisons which have hitherto guided us. Many elements which have never been obtained directly combined, are bound together by a third; thus we have no direct com-

pound of hydrogen and potassium, but in potassic hydrate an atom of hydrogen is united with oxygen, and an atom of potassium is united with this same oxygen HOK. Hydrogen in this hydrate is indirectly united with potassium, an atom of oxygen being the connecting link between them.

Some elements can be either directly or indirectly united with one another, and exhibit different properties in each condition. In organic compounds we know an immense number in which hydrogen is directly united with carbon. Thus, methylic oxide H_3COCH_3 has all its six atoms of hydrogen united with carbon directly, whilst vinic alcohol H_3CCOH has five of its

atoms of hydrogen united with carbon directly, and one atom indirectly, through oxygen.

In consequence of this difference, we find that the hydrogen, which is indirectly united with carbon through the intervention of oxygen, separates from it as soon as by any process the oxygen is replaced by chlorine or bromine; whereas the hydrogen which is directly united with carbon undergoes no change by such replacement. H_3COCH_3 by the action of PCl_5 becomes $\text{H}_3\text{CCl} + \text{ClCH}_3$, whereas H_3CCOH becomes H_3CCCl

+ ClH . When the hydrocarbons are liberated from these compounds, it is well known that a direct combination of carbon in one atom with carbon in another takes place, as in the formation of C^2H_6 from a methyl-compound, or $\text{H}_3\text{CCCCCH}_3$ from an ethyl-compound.

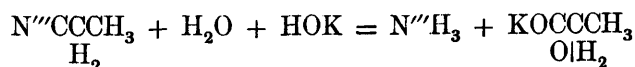
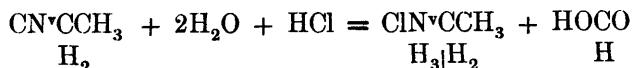
In like manner to oxygen, an atom of zinc holds two atoms of ethyl in combination in the molecule $\text{H}_3\text{CCZnCCCH}_3$, and by the action of water, the atom of zinc is replaced by two atoms of hydrogen, each atom of ethyl getting an atom of hydrogen in exchange for the half-atom of zinc which it held at first.

These and many similar reactions are now so familiar to chemists that I only allude to them to recall their bearing on the order of combination of atoms.

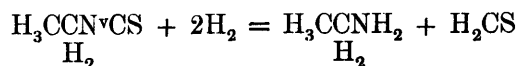
Not only are they known and admitted to be due to differences of arrangement, such as I have alluded to, but the idea which they have established is found a sure and faithful guide in the investigation of the intricate varieties presented by isomeric organic bodies in their varied reactions.

Thus it is well known from Hofmann's admirable researches on the isomeric cyanides and sulphocyanates, that, by the action of ethylia on chloroform, an ethylic cyanide is formed, isomeric with the compound formerly known. It breaks up by the action of hydric chloride in presence of water, into hydric formate, and the compound of ethylia and hydric chloride, instead of breaking up, as the other cyanide does, under the influence of alkalis, into ammonia and a propionate.

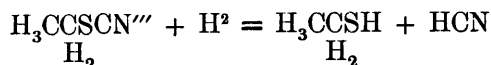
The following equations represent the two reactions:—



And in like manner his new sulphocyanates break up under the influence of nascent hydrogen, according to the equation—



whilst their isomerics on the SH_2 type break up thus:—



In the new cyanides, the carbon of the cyanogen is indirectly united with the carbon of the ethyl through an atom of nitrogen of the value 5; whereas, in the old cyanide of ethyl, the carbon of the cyanogen is directly combined with the carbon of the ethyl, and in the sulphocyanate carbon is indirectly combined with carbon through the intervention of sulphur.

What concerns us in these reactions is to see the evidence which they afford, that the binding element is an atom. The very fact itself amounts to that. In potassic hydrate, oxygen is combined with hydrogen; it is also combined with potassium, but the hydrogen cannot pass off, even at a red heat, in combination with its half of the oxygen. The two halves are inseparable, and when I say that in the molecule of potassic hydrate there is a single atom of oxygen, I merely state that fact.

I would gladly proceed now to other and certainly not less interesting considerations based upon the atomic theory, which

have received verification from experiment, considerations for which I think it would be at least rather difficult to find any equivalent if matter were not composed of atoms; but I must content myself with indicating them at present, and reserving for a future occasion the task of giving more development to them. I allude to atomic motion—the dynamics of chemistry. It has been shown that heterogeneous molecules, when mixed with one another in the fluid state, interchange their analogous constituents, and that the products thus formed, if they remain mixed in the fluid state, also exchange their analogous constituents, reproducing the original materials. In a solution of two salts there are formed two new salts by the exchange of bases; and it depends on the relative velocities with which the decomposing change and the reproducing change go on in the liquid, what proportion the quantity of the original materials bears in the final mixture to that of the new products.

In using the atomic language and atomic ideas, it seems to me of great importance that we should limit our words as much as possible to statements of fact, and put aside into the realm of imagination all that is not in evidence. Thus the question whether our elementary atoms are in their nature indivisible, or whether they are built up of smaller particles, is one upon which I, as a chemist, have no hold whatever, and I may say that in chemistry the question is not raised by any evidence whatever.

They may be vortices, such as Thomson has spoken of; they may be little hard indivisible particles of regular or irregular form. I know nothing about it; and I am sure that we can best extend and consolidate our knowledge of atoms by examining their reactions, and studying the physical properties of their various products, looking back frequently at the facts acquired, arranging them according to their analogies, and striving to express in language as concise as possible the general relations which are observed among them.

In conclusion I must say that the vast body of evidence of the most various kinds, and from the most various sources, all pointing to the one central idea of atoms, does seem to me a truly admirable result of human industry and thought. Our atomic theory is the consistent general expression of all the best known and best arranged facts of the science, and certainly it is the very life of chemistry.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Thursday, November 4th, 1869.

SIR BENJAMIN C. BRODIE, Bart., F.R.S., in the Chair.

THE minutes of the previous meeting having been read and confirmed, the following certificates were read:—

For the first time—Sir Roderick Impey Murchison, Bart., Belgrave Square; John Wiggan, Pharmaceutical and Analytical Chemist, Ipswich; George Harrison, Analytical Chemist, 26, Havelock Square, Sheffield; Thomas Walton, M.R.C.S., and L.S.A., Lecturer on Chemistry at the Hull and East Riding School of Medicine, Kingston-upon-Hull; Edward Smith, Practical and Pharmaceutical Chemist, Strand, Torquay; G. Manley Hopwood, 22, Grosvenor Square, All Saints, Manchester; Thomas Gibb, A.R.S.M., Engineer; Matthew H. Cochrane, 108, Paul Terrace, Glasgow.

For the second time—E. S. Blackwell, Analytical and Consulting Chemist, 6, St. Sacrament Street, Montreal, Canada.

For the third time—Alfred Dudley Keightley, Gatcheck Gunpowder Mills, Old Hall, Milnthorpe, Westmoreland; W. Fletcher Barrett, Lecturer on Physical Science at the London International College; John Morrison, Analytical Chemist, County Wicklow, Ireland; Temple A. Orme, Teacher of Chemistry and Experimental Physics in University College School; W. G. Lewis, Fellow of Oriel College, Oxford.

The last-named gentlemen were ballotted for and duly elected. Mr. Gerstl was elected an Associate of the Society.

The CHAIRMAN said the first business before the Society was to consider a paper "*On the Atomic Theory*," which had already been read before the Society by Professor Williamson. This theory was not to be regarded as a fixed and definite system of ideas, but one that had undergone great variation and change. There was the atomic theory of Dalton; then that of Berzelius, and also, in a certain sense, that of Laurent and Gerhardt; and now they had come to a further form of this theory, in which new ideas had arisen in regard to the nature of atoms and their properties; and he (the Chairman) thought it would greatly facilitate the discussion if Dr. Williamson would explain what was the precise form of the atomic theory which he was prepared to maintain and defend, and how they might discriminate that from other forms of the theory which were neither reasonable, nor rational. First, there was the question whether there were atoms at all; then, being atoms, what those atoms were, and whether they were endowed with the properties assigned to them in regard to their replacing power, and to what was termed, their value.

Professor WILLIAMSON, on rising, said that he did not admit that, among chemists, there had been several atomic theories. If there had been, he had yet to learn of them. There had prevailed, he believed, from time immemorial, a belief that matter was built up of small particles; and he might also say that no contrary opinion had ever been embodied in any definite form. Dalton doubtless looked for evidences of what he believed to be true, and saw, in the simple multiple proportions which he specially alluded to, facts which were in accordance with that preconceived conviction; but his was the mere germ of an atomic theory, and the changes which have taken place in it since are consistent with the original notions. The very rapid changes had, in the main, been additions to the starting-point given by Dalton. The line of work so vigorously pursued of late years by

many chemists, regarding the order in which atoms are arranged in their compounds, was mentioned by the speaker. His endeavour had been to put together more fully than had been done of late what is known of the chemical evidence; firstly, respecting the limits to the divisibility of matter, and, secondly, with regard to the properties of those finite particles which constitute the limits of divisibility, solely from the point of view habitually employed by chemists in their ordinary working. He had also endeavoured to separate those conclusions which appeared to him warranted by facts from everything else. Whether the smallest particles of matter had a spherical form or not, whether they were in their nature indivisible, whether they were in reality the ultimate atoms of matter, or like the planets of this system, he knew not, nor did such questions exist for him as a chemist. He therefore thought it wise to exclude them, important as they were, from the actually existing atomic theory. The work of Berzelius was perhaps the most significant transition from the original notion of Dalton. Silently these atoms had been accepted by chemists, and the whole course of investigation had been one grand confirmation of the assumption that compounds must have molecular weights corresponding to at least the smallest atomic proportion which would represent the actual numbers of analysis. The perfectly independent observations which had been made in reference to: the boiling points of homologous liquids, the phenomena of diffusion, the equality of volumes of masses containing an equal number of these molecules under similar conditions in the gaseous state, all concurred to corroborate the conclusions necessitated by the atomic theory. Thus, independent workmen hewed stones which, when hewn, were found to fit in exactly with the others, forming a perfectly homogeneous whole. Dr. Williamson concluded his remarks by referring to the atomic values, a term which, he thought, represented in a more precise way than some others what is called atomicity; and he also referred to the difference between direct and indirect combination, a fact which he conceived to be essentially atomic in its nature.

Dr. FRANKLAND was not present when Professor Williamson delivered his lecture, and he had only cursorily looked over the printed memoir; but, so far as he could gather, the object of the author had been to establish the atomic theory as an absolute truth. There had been, he thought, so little, if any, opposition to the application of the atomic theory to the phenomena of chemistry, that a discussion could scarcely be raised upon any other feature of the question than that of its absoluteness. He considered it impossible to get at the truth, as to whether matter was composed of small and indivisible particles, or whether it was continuous—the question belonged to what metaphysicians termed "the unknowable;" but he acknowledged the importance of the fullest use of the theory as a kind of ladder to elevate the chemist from one position to another in his science. He was, however, averse to accepting the theory as an absolute truth. Any attempt to realise by its help the action of attractive or repulsive forces upon matter was excessively difficult, indeed to realise such an action through a perfectly void space was to him quite impossible. The same difficulty presented itself to Faraday, who was often obliged to throw on one side, as an obstacle to his progress, this atomic theory. He said that if matter be assumed to be thus composed of solid particles separated by a void space, then, in considering the phenomena of electricity in connection with that view of matter, this space existing between the atoms must be either a conductor, or a non-conductor of electricity. If a conductor, such a thing as an insulator was obviously an impossibility; if it was a non-conductor, such a thing as a conductor was equally inconceivable; so that, apart from chemistry, there were considerations which made it very undesirable for this theory to be represented as an absolute truth. The speaker then referred to the combination which, in certain cases, is effected between gases by the application of heat,

and said that, according to the atomic hypothesis, they must assume that the gases, when heated, have their particles driven further asunder; but how, then, could they more readily enter into combination when heated, as was the case with oxygen and hydrogen, and in many other similar instances? No such difficulty presented itself if the gases were regarded as continuous matter. He admired the theory as much as Professor Williamson, and he thought no one could blame him for not making a sufficient use of it; but he did not wish to be considered a blind believer in the theory, or as unwilling to renounce it if anything better presented itself to assist him in his work.

Dr. ODLING, as a chemist, was not particularly interested in the question whether matter was infinitely divisible or not, but he did not think that Dr. Williamson's argument had established that conclusion. Dalton was always spoken of as the discoverer of the law, or doctrine, or theory of combination in definite and multiple proportions, to account for which his invention or adoption of the atomic theory was founded; and he conceived Dalton's great discovery to be better expressed as the law of combination in *reciprocal* and multiple, instead of in *definite* and multiple, proportions. Dr. Williamson had said of chemists that all their modes of thought, and all the government of their actions, was based upon the atomic theory; but he (Dr. Odling) maintained that it was based upon the observed fact that certain bodies combined in certain proportions. Dr. Williamson also argued that the atomic theory was based upon the existence of molecules, and that molecules had no *locus standi* in the absence of the atomic theory. He (Dr. Odling) disputed that position, for the fact that the hydrogen existing in marsh gas was divisible into four parts, and the hydrogen existing in ammonia only into three parts, was, he conceived, a fact quite independent of the atomic theory. The laws of combination, as far as they go, were compared by Sir Humphry Davy to Kepler's laws of planetary motion, which were simply a general expression of observed facts; and, in the same way, these laws of chemical combination were general expressions of observed facts upon which the atomic hypothesis was super-induced.

Professor MILLER thought that Dr. Odling's arguments had not disproved the atomic theory; if they had not the atomic hypothesis, they were entitled to ask what explanation they possessed of the laws of combination? Certain facts were admitted on all hands, as determined by experiment, and when an important and extensive series of facts was ascertained, the endeavour to explain them by some supposition which embraced the facts, and which enabled them to anticipate new ones if possible, was a necessary result of their mental constitution. Unless some hypothesis were accepted, it was absolutely impossible to reason upon the facts; and if they could not adopt this hypothesis as absolutely true, such a view of the constitution of matter explained all the chemical facts that had hitherto been presented. It appeared to him that those who denied the atomic hypothesis were bound to supply something to enable them to interpret phenomena with the same regularity and order as the hypothesis, the accuracy of which they denied and desired to displace. No one would suppose that the absence of an undulatory theory for light would conduce to the explanation of optical science; and he held that what the undulatory theory was to the phenomena of light, the atomic theory was to the phenomena of chemistry.

Professor FOSTER thought the question before them was not so much the utility of the atomic theory as its truth. M. Naumann had stated, in his "Relations of Heat to Chemistry," that, if we assumed that in any compound body the components really occupied distinct portions of space, they must assume that body to be incapable of infinite divisibility. He thought the ideas generally entertained of the existence of the constituents of bodies in compounds were not absolutely necessary ideas. The fundamental phenomena of chemical changes

might sometimes be explained by returning to the notion of the actual mutability of matter. By operating upon one portion of matter, it was actually transmuted into another, a qualitative and quantitative relation existing between the disappearing and the appearing bodies. From such ideas as these, they could not deduce the necessary existence of atoms; but all our present modes of expression and modes of thought were founded upon an atomic hypothesis or basis.

Professor TYNDALL sympathised with the ideas of Professor Williamson; his thoughts had, to some extent, been expressed by Dr. Miller, who had made a strong point in referring to the undulatory theory. That theory was something super-induced upon the facts, which might be readily detached from the theory. But it was in the nature of the human mind, it was in the nature of a profound thinker, when pondering upon facts of this nature, to seek for some underlying principle outside the region of facts, from which the facts followed as consequences. Dr. Odling ought to have gone a step further than Kepler; for something that we now call "the theory of gravitation" was certainly super-induced upon his facts, as the atomic theory is upon the facts of multiple proportions. Professor Foster had justly referred to the consideration that a bad theory was very often useful. The emission theory of light was useful in the hands of Newton, Laplace, Malus, and Brewster; but this theory fell, because, in the progress of investigation, facts arose which were inexplicable by it, and which were completely explained by the undulatory theory. The undulatory theory would successfully front all opposition as long as it was competent to explain the facts of optics; and he apprehended that the atomic theory would stand as long as it was competent to explain the facts of chemistry.

Dr. MILLS's conviction was that chemistry had no facts to support the notion of a limit, and the undulatory theory had an immense advantage over the atomic theory, for the existence of waves was a fact, while the existence of a limit was not a fact. It seemed to be forgotten by many writers that matter might be infinitely divisible, and yet that definite proportions might exist, for between two infinities there might be a finite ratio, so that the atomic theory was not perfectly necessary to chemistry. He believed that motion was the highest generalisation of modern science, and it therefore afforded the only criterion by which all theories, including those of chemistry, must be judged, and the notion of a limit was practically inconsistent with the idea of a motion.

Dr. WILLIAMSON, in his reply, remarked that the benefit accruing from looking at the question from another point of view would be incalculable, and if another view was developed to supersede the present one, he would be among the first to rejoice at it, but he had not to do with the future of this matter. He had endeavoured to put together the actual evidence of the present view, and none of its opponents had been able to find a fallacy in that evidence. He thought it most important to keep the theory at each period of its growth in the modest position which it at present occupies, that of generalising the best-ascertained relations of the elements in their chemical changes.

The CHAIRMAN liked to have clear and definite ideas, as far as he was able to realise them, on scientific subjects, and he was unable to consider even an atomic theory in the abstract. The atomic theory, as he understood, was—that matter is made up of finite particles, the aggregate of which could be divided and subdivided until at last only one particle would remain, and this view might be derived from the perusal and common assent of every work on Chemistry that defined the atomic theory. He thought that such a view as the physical indivisibility of matter must be separated from the facts and basis of chemistry. Dr. Williamson seemed to think the theory and facts were one, but he (the Chairman) asserted that they were two distinct things. He must also express his dissent from the views expressed by Drs. Frankland and

Miller, with reference to the use of a doctrine or theory in which they did not believe. He could not understand using a theory and denying it at the same time. This theory had, he thought, been often the means of deluding chemists into the belief that they understood things about which they knew nothing. He found the works of Kekulé and Naquet scribbled over with pictures of molecules and atoms, combined together in all imaginable ways, for which he thought there was no adequate reason, and if there was no reason it was a mischievous thing to do. Many students, he believed, thought the pictures in Naquet's work were chemistry; they did not draw the distinction between the facts and theory of science. His view was that the ultimate constitution of this material universe was one of those things upon which no light had yet been thrown, and he agreed with Dr. Odling when he said that the science of chemistry did not require or prove the atomic theory. They were bound to have some real and adequate means of working at the science of chemistry, and discovering its laws, and they could effect this either through the investigation of the laws of gaseous combination or the study of the capacity of bodies for heat. When they approached the science through the study of gaseous combinations, they discovered that the combining proportions of bodies were capable of being represented by integral numbers, and they also found an analogous fact in studying the capacity of bodies for heat.

The meeting was then adjourned to November 18th.

NOTICES OF BOOKS.

Nature: "A Weekly Illustrated Journal of Science."
MACMILLAN and Co., London.

WE are glad to notice the birth of a new popular journal of science. It was never more wanted than now, for it is undeniable that at no previous period has there been such a manifest desire on the part of the general public to understand somewhat of the great scientific discoveries and generalisations which are perpetually springing up around us. Among the objects proposed to be attained by "Nature," is the urging "the claims of science to a more general recognition in education and daily life," and we are fain to believe that there is now amongst us such a movement in this direction, emanating from diverse sources, that the time is not far distant when science will form as much a part of our own educational system as it does of that of other countries.

"Nature" appropriately opens with a series of aphorisms by Goethe; a semi-poetic composition, formed as it were, halfway between prose and poetry, in which an exalted form of prose almost merges into a regular rhythmus. Of Nature Goethe says:—"She tosses her creatures out of nothingness, and tells them not whence they came, nor whither they go. It is their business to run, she knows the road. . . . Her crown is love. Through love alone dare we come near her. She separates all existences, and all tend to intermingle. She has isolated all things in order that all may approach one another. . . . She is complete but never finished. As she works now, so can she always work. Everyone sees her in his own fashion. She hides under a thousand names and phrases and is always the same."

The principal papers are "On the recent total eclipse of the Sun" by J. Norman Lockyer, and "On the fertilisation of Winter Flowering Plants" by A. W. Bennett. There is a review of Madsen's *Antiquités Préhistoriques du Danemarck*, by Sir John Lubbock, and of Newman's "British Moths," by W. S. Dallas, and other shorter notices. A paper (read at the last meeting of the British Association for the Advancement of Science), by the Rev. W. Tuckwell "On Science-teaching in Schools" contains a number of very useful suggestions, and will be read by

science masters with interest. Professor Williamson furnishes an interesting life of the late Professor Graham, and we wish we could commend the accompanying portrait to a like extent. Mr. Geikie, gives an account of the meeting of German naturalists at Innsbruck. Among other features of the Journal we find several columns of "Notes," containing a chit-chat account of the matters most discussed in scientific circles at the present time. Finally, there is a *resumé* of recent work in all the more prominent branches of science, and of the proceedings of Societies and Academies. We wish "Nature" every success; it is well supervised, its contributors are manifold, and it is issued by an eminent firm of publishers. It will be a healthy sign of the times and of progress, when every educated man reads a scientific journal as regularly as he reads his "Saturday" or "Pall-mall," and to such a result the issue of "Nature" conduces.

MISCELLANEOUS.

University of London.—The following are lists of the candidates who have passed the Second B.Sc. Examination:—*Pass Examination.*—First Division. William Henry Johnson, University College; Alexander Muirhead, University College; William Stephen Ridewood, B.A., private study. Second Division. Phineas Simon Abraham, Trinity College and Royal College of Science, Dublin; William Barnett Burn (First M.B.), St. Bartholomew's Hospital; Dan Isaac Davies, private study; Septimus Peché Moore, LL.B., New and University Colleges; Frederic James Montague Page, Royal School of Mines; Frederick Antony Potter, Royal School of Mines; Charles Thomas Whitmell, St. John's and Trinity Colleges, Cambridge; William Henry Willans, University College and Royal School of Mines.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

In accordance with the generally expressed wishes of our friends and readers, we have effected arrangements to enable us to give, under the above heading, notices of EVERY CHEMICAL PAPER IN THE WORLD, as soon as possible after publication. Whenever possible, these notices will appear in the form of carefully prepared, although necessarily brief, abstracts; as respects papers either too long or too abstruse to render condensation possible, their titles will be chronicled; and in all cases accurate reference will be made to the original publication. The two half-yearly volumes of the CHEMICAL NEWS, with their copious indices, will therefore be equivalent to an English edition of the "Jahresberichte," with the additional advantage of keeping the readers week by week on a level with the latest advances of science.

NOTE. All degrees of temperature are Centigrade, unless otherwise expressed.

Comptes Rendus des Séances de l'Académie des Sciences, November 2, 1869.

This number contains the following original papers and memoirs:—**Industrial Use of Mineral Oils for the Purpose of Heating Steam Boilers, and particularly Locomotive Engines.**—M. St. Claire-Deville and Dieudonné.—This paper gives an interesting account of a series of experiments made by the authors with locomotives upon the French Eastern Line (Paris to Strasbourg), with a speed of 46 kilometres (about 29 miles) per hour, and upon a portion of the line of railway which is by no means level. The consumption of mineral oil was from 3.44 to 5 kilos. per kilometre, over a total distance of 142 kilometres, run over with heavily-laden trains. The authors state that the combustion was very complete.

Heating of Wines.—M. Thenard.—This subject, which has been repeatedly before the meeting, seems to have given rise to some jealousy, as well as captious controversy. The author of this paper, acting upon the principle "*Qui bene distinguit bene docet*," states that M. Appert first discovered the principle, that M. Pasteur has given a proper scientific explanation thereof, and that, lastly, M. Vergnette has been the first man who has industrially applied this principle on the large scale with good success.

XV. *On Statical and Dynamical Ideas in Chemistry.*—Part. III.
The Atomic Theory. By EDMUND J. MILLS, D.Sc.*

CONTENTS.

Introductory Remarks. Primary postulate of the atomic theory. Dalton's views. Atomic motion. The singular relations of formulæ and symbols neither suggest nor prove the existence of indivisibles; the equatorial method leads only to a least common multiple. Instances of the supposed explanation of isomerism on atomic principles: chemical structure. Definite proportions may be consistent with infinite divisibility, and are consistent with continuity: illustrations. Absence of evidence that matter and division are mutually related: appeal to philosophy necessary. Digby's proof that there are no parts in quantity. The atomic theory shares in the fallacy of materialism,—and of the absolute, so far as that is fallacious. Actual realization of the atom: parallel from phlogiston. Instances of uncertain and contradictory results. Opinions of Newton, Descartes, Leibnitz, Kant, Davy, Wollaston, and Faraday. Nature of the issue.

A CRITICAL examination of some of the leading ideas relating to Chemical Functions and Chemical Substance†, conducts, by an easy and simple transition, to a discussion of the Atomic Theory. If the reader will admit as sound the characteristic of a universal criterion pointed out in Part I., he may now feel an interest in reading the oldest legend of systematic physics by the light of the latest and best development of modern science. The idea of motion, which is the criterion in question, comes inevitably to be accepted as the sole reliable guide, when a guide is sought in scientific controversy: it does not appeal to nor is it derived from this or that authority; but, as the common property of every one who reflects, and drives his conclusions to their end, it is immediately and independently available.

The primary postulate of the atomic theory is the existence of indivisibles. From this demand it has never receded, whatever may have been the state of contemporary science. From Lucretius, whose lines

Hæc neque dissolvi plagis extrinsecus icta
 Possunt; nec porro penitus penetrata retexi;
 Nec ratione queunt alia tentata labare. [I. 531–533.]

[Nor, struck with outer blows, can these dissolve;
 Nor, penetrated deep, be disentwined;
 Nor, tried in other mode, can waver aught.]

are explicit upon this point, to the majority of modern chemical writers, this supposition pursues an undeviating course. Upon the different properties of these indivisibles, however, all their

* Communicated by the Author.

† Phil. Mag. S. 4. vol. xl. p. 259.

defenders are not agreed. Dalton, for example (New System, pp. 135, 136), conceives water to have an internal constitution resembling square piles of shot arranged in successive horizontal strata. "A vessel full of any pure elastic fluid" also "presents to the imagination a picture like one full of small shot" (pp. 147 & 189). When two gases are mixed, an intestine motion ensues, and continues "till the particles arrive at the opposite surface of the vessel against any point of which they can rest with stability, and the equilibrium at length is acquired when each gas is uniformly diffused through the other" (p. 190). Solids likewise consist of arranged particles (p. 209). Hence it is evident that Dalton regarded atoms as enjoying a perfect repose, unless when mechanically or chemically disturbed. In this purely statical contemplation he has been followed by most chemists, some of whom have believed themselves to dissent wholly from his theory. What is the theory of types, but an emanation from the prime idea involved in the celebrated figures at the end of the 'New System'? The wooden models with which Dalton illustrated his lectures have reappeared as glyptic formulæ; and the material existence of their connecting wires is perpetuated in the lines or "bonds" of graphic formulæ.

But atoms have been considered from another point of view. It has been found by not a few thinkers that rest is a condition which falsely represents the facts of nature, and that atoms must therefore be conceived as moving with an industry to which cessation is unknown. On this view, the state of dissolved salts and the process of precipitation are explained much as Berthollet explained them, only in corpuscular language. Supposing, for example, hydric chloride be added to aqueous cupric sulphate. That cupric chloride is formed is shown by the green coloration that ensues. Hence there has been a partition of the copper. This is accounted for by supposing all the atoms in the mixture to move constantly—by adopting, in short, the theory of greatest effort. Another chemist observes that if all the atoms were perfectly free to move, no compound could be stable, and consequently brings forward an hypothesis of "limited atomic mobility."

Considerations derived from chemical formulæ have frequently been adduced in favour of the atomic theory, and therefore deserve attention. The formulæ themselves were at first the results of experimental facts in quantitative analysis, and are therefore independent of theory. Dalton first applied a method of symbolic ratios, in which attention was especially drawn, first, to a standard unit for each element, and secondly to that unit's coefficient. The standard unit is then taken as the atom; a necessary consequence of which supposition is, that all coefficients must be integral. It will be observed, however, that we are now

Phil. Mag. S. 4. Vol. 42. No. 278. Aug. 1871.

I

no longer dealing with fact but with a crude conjecture; and the well-known rules given by Dalton for ascertaining the complexity of a combination, and intended to develop his system of ratios, are more conjectural still:—If only one combination of two elements exist, it must be presumed to be binary; when three combinations are obtained, we may expect one to be a binary, and the other two ternary, and so on*. Berzelius himself felt enamoured of the theory, and occasionally turned aside from the path of induction to guesswork of a similar kind:—Strong bases consist of a radical taken once, combined with oxygen taken once†; and, “if a combustible radical‡ unite with oxygen in several proportions, these are compared, and the result is reduced to the smallest number of atoms possible.” With the introduction of the word *equivalent* by Wollaston, the symbolic unit acquired a new implication; and the historical reader is familiar with the confusion produced and maintained for very many years by this insertion of a peculiarly dynamical idea in the ungenial soil of contemporary speculation. Writers of text-books failed to understand their position; and the science was still struggling underground when the splendid discovery of Dulong and Petit gave it vigour and foliage. This discovery, indeed, was left to other hands to improve or perfect; but by the distinct relation it evinced between the symbolic standard and specific heat, decision and certainty were able to displace conjecture. Another important step was to adopt a uniform understanding as to the relation of composition to specific gravity of vapour, this understanding having been based upon formulæ which had been determined by the previously existing canons. The indications afforded by isomorphism are of minor value. But throughout these various processes—establishing by analytical comparison certain standard units and ratios, discovering that certain of these were connected with the specific heat by a simple law, that to these a uniform vapour-volume may be assigned, and that similarity of chemical function frequently involves similarity of form (another function)—where does indivisibility suggest itself? Still less is the existence of an atom *proved*.

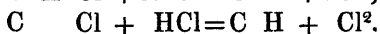
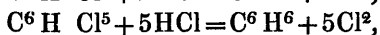
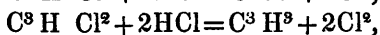
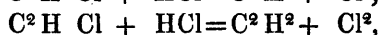
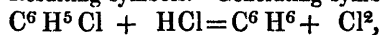
I now pass from the singular relations of formulæ to consider them as existing in equations. Let it be required, for instance, to find the formula of benzol. The values $C=12$, $H=1$ are given. The analytical result, in terms of these values, is CH . Recourse is then had to chlorination, which occurs, or may be taken to occur, in successive stages; the product at each stage is analyzed ($Cl=35.5$), and the corresponding minimum equations are written thus:—

* New System, p. 214.

† *Traité de Chimie* [Esslinger], vol. iv. p. 604.

‡ *Théorie des Proportions Chimiques* (1819), p. 117.

Resulting symbols. Generating symbols.



The passage from chlorine derivative to parent compound is effected by the numerical exchange of Cl for H, the validity of which need not be disputed, though it is often much misunderstood. We then have four formulæ— $\text{C}^6 \text{H}^6$, $\text{C}^3 \text{H}^3$, $\text{C}^2 \text{H}^2$, $\text{C} \text{H}$ —between which to choose. Now the equational method, if I may so term it, does not exactly choose between these, but *takes the least common multiple of them*, and, *on that ground*, decides on $\text{C}^6 \text{H}^6$ as the formula of benzol. The doctrine of replacement in successive stages (as, for instance, the treble ethylation of ammonia) is substantially identical in its symbolic exposition with the equational method. Now this method is held to point out that the “atom of benzol weighs $\text{C}^6 \text{H}^6$.” Is it necessary to indicate that the use of the process for finding the least common multiple is not atomic, and that, if so, arithmetic should also possess its atomic theory?

If the prejudices of education were less complete or less closely intertwined than they are, I might hopefully ask atomic theorists whether, as professedly inductive reasoners, they are still pleased to accept these shadows for reality. My argument may have a better fortune, perhaps, with those who sit loose to theory, or at least will not voluntarily put on the shirt of Nessus. Accordingly, it may be advantageous if, after proceeding from the construction of symbols to equations, we visit the atomic theory in a spot that is peculiarly its home, namely the province of isomerism. It is here that, we are told, the greatest victories of that theory have been won, that it is of the highest practical utility, and where, without it, we can conceive no other guide to an explanation*. The following special case, which, I believe, has no exceptional features, is selected from Kekulé's *Lehrbuch* (vol. ii. pp. 257, 258), and relates to the well-known instances of the two isomers $\text{C}^4 \text{H}^4 \text{O}^4$, and the three isomers $\text{C}^5 \text{H}^6 \text{O}^4$. These bodies, which are known as fumaric and maleic acid, and itaconic, citraconic, and mesaconic acid, respectively, unite each with the same quantity, of hydrogen to form succinic acid, $\text{C}^4 \text{H}^6 \text{O}^4$, and pyrotartaric acid, $\text{C}^5 \text{H}^8 \text{O}^4$. Each of the isomers combines also with the same weight of bromine; but, contrary to expectation (based on the hydrogenating experiments), two dibromosuccinic acids,

* British Association Report for 1870: Transactions of Sections, p. 45.

$C^4 H^4 Br^2 O^4$, and three dibromo-pyrotartrates ($C^5 H^6 Br^2 O^4$) are formed. We have therefore to explain how it is that these facts, assuming them to be true, are compatible with each other. Kekulé proceeds as follows:—

“In accordance with the views relating to the atomicity of the elements which we have previously unfolded on several occasions (see especially § 1369), all the affinities of the atoms comprising the molecule of succinic (or its homologue pyrotartaric) acid are saturated; these acids constitute, in a manner, closed molecules. They contain two atoms of typical oxygen, that is, oxygen bound on to carbon by only one of its two units of affinity. Two hydrogen atoms are united with the carbon only through the intervention of these typical oxygen atoms. These two typical hydrogen atoms are easily displaceable by metals; but there are two other oxygen atoms present which are attached to the carbon by two units of affinity, and consequently, in the language of the type theory, belong to the radical.

“Now, it is easy to see that, in addition to these two typical hydrogen atoms, succinic has four, and pyrotartaric acid six, more atoms of hydrogen. This hydrogen, which in the language of type theory belongs to the radical, is, according to the theory of the atomicity of the elements, directly combined with the carbon—in fact, in such a manner that two hydrogen atoms are always united with the same carbon atom.

“Next, let us assume that two such hydrogen atoms are absent (*fehlen*) from one or other of these two normal acids; we have, on the one hand, the composition of fumaric and maleic acid, the formulæ of itaconic, citraconic, and mesaconic acid on the other. But since in succinic acid two pairs of such hydrogen atoms are bound to the carbon, two acids may evidently exist with less hydrogen; and similarly, in the case of pyrotartaric acid, we can understand how there may be three isomers with less hydrogen, according to the absence of one or other of the three pairs of hydrogen atoms, which in the normal substance are directly united with the carbon.

“At that place in the molecule whence the two hydrogen atoms are absent, two units of affinity of the carbon are left unsaturated; at that place there is, so to speak, a gap. Hence we can explain the exceptional facility with which these substances unite, by way of addition, with hydrogen or bromine. The free units of affinity of the carbon make an effort to saturate themselves, and so to fill up the gap.

“If hydrogen be introduced into these unoccupied spaces, all carbon atoms within the molecule are united to the same element—hydrogen; there appears no ground for the existence of differently modified normal substances as so obtained. In

fact, only *one* succinic and *one* pyrotartaric acid are at present known.

"If, on the other hand, bromine be put in those same unoccupied spaces, the carbon within the molecule is partly united with hydrogen, partly with bromine; and it is readily perceived that different modifications of such bromo-acids must necessarily exist, according as the bromine finds itself in one or the other of those spaces."

This mode of explanation is now virtually common to all atomic theorists. It is assumed that substances consist of molecules, these again of atoms; that determinate space or position (*Stelle*) is conceivable without atoms, and exists indeed in their absence; and that into this space there stretch at all times mysterious units of affinity, which, when the atoms are no longer present, strive after combination. But if all chemical substances consist of atoms, and position is possible without them, how can such position be known or determined? According to Hegel, pure being is pure nothing; and we may assign pure position to the same category. But determinate space or position, with the only thing that can determine it taken away, is contradiction itself. Still more unsatisfactory are the units of affinity (*Verwandtschaftseinheiten*). They cannot be chemical substance, or they would be identical with the atom; they cannot be dynamical units, similar to foot-pounds, for no such integral relations as they would then present have been found in the measurements of chemical action. Yet unquestionably dynamical language is used of them; they are said "to make an effort," "to bind on," "to rivet together," &c. It is much to be deplored that no atomic theorist has yet thrown light on the obscure question of units of affinity, or even stated in clear terms what he means by them. In the absence of any such statement, I shall class them, as pure number, in the roomy category of Hegel.

If any one were to observe under a microscope a small insect with cephalic, thoracic, and abdominal appendages, and were afterwards to assert that these were six in number, there being two of each name—that he had removed two of them, which the insect made a proportionate effort to reunite to its body, and that as the remaining four were removed an increased struggle was manifest—such statements, I say, would be conceivably true. But when language like this is used to explain to me the "structure" of a succinate, I decline to accept either its substance or its form, until the facts alleged of the succinate are put upon the same footing as those asserted of the insect. Until then, "units of affinity" may be considered as false an expression as "units of hunger" would be now.

Kekulé himself, by admitting a class of isomers "im engeren

Sinne," has tacitly shown the weakness of the atomic interpretation of isomerism.

Those who consider isomerism explained by such methods as have just been discussed, must understand by an *explanation* something different from the scientific meaning of that term. A phenomenon is explained when it is shown to be a part or instance of one or more known and more general phenomena. Isomerism is not, therefore, explained by assertions about indivisibles, which have neither been themselves discovered nor shown to have any analogy in the facts or course of nature—nor by explicit statements about a "structure" which has never been seen—nor by the use of a phrase to which no clear definition has been, or can be, attached.

Before isomerism had acquired the importance it now possesses, the great argument in favour of the atomic theory was that the law of multiple and that of definite proportions undeniably represent facts which can be explained only by the existence of atoms. Here the inadequate and idle notion of an "explanation" recurs. I have already (p. 115) exposed the fallacy of supposing that the equational method of arriving at formulæ is any thing more than the arithmetical process of taking the least common multiple—and pointed out the imaginary nature of Dalton's rules (p. 114); and formulæ that have been obtained by these means, in order to affirm the law of multiple or definite proportions, are condemned accordingly. But the exact point of this argument, so far as it has not been alluded to already, lies in the following considerations. Supposing an aqueous solution of hydric chloride be mixed with successive small quantities of sodic hydrate. Several actions occur; but consider for a moment only that one whereby the hydrogen of the hydric chloride is exchanged for sodium. It is quite evident that, on each addition of the sodic hydrate, a new compound ought to be produced containing, say, the whole of the sodium, in the form $H_xNa_yCl_z$; and as the quantity of the sodium may be varied infinitely at pleasure, an infinite variety of hydrosodic chlorides must, if matter be infinitely divisible, be the result of the process. But not only does such a variety not arise, there is a perfect absence of any hydrosodic compound; for the sole product of the reaction in every case is sodic chloride, $NaCl$. Hence it is inferred that matter cannot be infinitely divisible—that there has been a *saltus*—in short, that atoms exist.

Now this is a question of a constant ratio considered as existing between sodium and chlorine when brought together under conditions which need not be constant. As the mixture is made, the sodium and chlorine are unquestionably divided by being dissolved in a larger quantity of liquid than before. If

10 grammes of sodium were originally present, they now consist of two lots of, say, 5 grammes each. This makes it quite conceivable that, without the addition of any more of the solvent, the division may continue of its own accord, say, into ten lots of 1 gramme each, a thousand lots of a decigramme each, and so on, without limit. The same is true of the chlorine. On endeavouring to prepare a compound from the solution, only one is obtained with an invariable ratio between the sodium and the chlorine. The reason of this phenomenon is presumed to be unknown and to be now sought. I can only say that the fact, from the above point of view, is as conceivable on the supposition of continuous as it is upon that of limited division. Two phenomena continuously proceeding without obvious end (mathematical "infinities") are well known to be capable of a finite ratio. Through one point an infinite number of curves may be drawn. The neutralization of aqueous hydric chloride is something like the process of differentiation, and its result, a constant finite ratio, like a differential coefficient. Or take as an illustration the properties of the machine known as the "geometric chuck." By a suitable combination of circular movements, this beautiful instrument is capable of describing an endless variety of curves, one of which is roughly represented in the margin: such a figure is drawn by a motion which is visibly continuous, even at the three points, throughout the entire period of delineation; when it has been described, the machine proceeds to draw an exactly similar triangle, which it accurately superimposes on the first, and so on, to any number of triangles. The number of points in the figure is regulated by previous adjustment of the constants of the machine; but the mass of the instrument, its rate of motion, and the number of times it is resolved (beyond the construction-minimum) have nothing to do with the resulting figure. The definite proportions of chemistry, in like manner, precede or accompany each of our experiments; they are independent of mass, rate of action, repetition of action; and doubtless they are produced, like these points, by compound uninterrupted motion. They certainly suggest nothing that is by nature atomic. These mathematical conceptions, however, involve no breach of continuity, which is rather their essential condition; and the chemical phenomenon is at least as conceivable as they are without introducing the supposition of a limit.



I may adduce the process of diffusion as one that, in accordance with the large number of experiments already made, is probably capable of continuance without any clear reason for a limit. Yet if matter consisted of indivisibles, some sign, at any rate, of

a limit ought to have been by this time detected. The continuity of the gaseous and liquid states furnishes a strong experimental presumption against any kind of constitution of matter, corpuscular or otherwise. The atomic conception of definite proportions is therefore not only not absolutely necessary, but doubly improbable.

The law of definite proportions, indeed, is itself tinged with continuity. It represents one side only of the series of bodies, which includes mechanical mixtures on the one hand, definite compounds on the other, and indefinite substances (like albumen) as its middle term. Even should much more refined methods of determining a symbolic value be discovered than we now possess, the law of homology is an instant prophet of their weakness; starting with almost perfect definition, it ever points to some possible transcendent complexity.

Such is the nature of the arguments involved in ratiocination upon a materialistic basis. Matter, it is asserted, must be either infinitely or finitely divisible, as if either conception had ever been realized by the interlocutor. What if matter do not exist at all? And if it exist, where is the proof that it and division have any mutual connexion whatever? It is these prior questions that chemists, as a rule, never raise, or dismiss as fruitless—forgetting that in philosophy, the storehouse of the most general propositions of all the sciences, they have their only court of appeal. Under the impression of these convictions, I now proceed to give an abstract of Digby's* most able argument on the nature of quantity, a subject which evidently involves the atomic theory among its component questions.

In the first place, Digby investigates the meaning tacitly or otherwise assigned to the idea of quantity by the learned as well as the uninstructed. "If you ask what quantity there is of such a parcell of cloth, how much wood in such a piece of timber, how much gold in such an ingot, how much wine in such a vessel, how much time was taken up in such an action? he that is to give you an account of them measureth them by ells, by feet, by inches, by pounds, by ounces, by gallons, by pints, by dayes, by houres, and the like; and then telleth you how many of those parts are in the whole that you enquire of. . . . Wherefore, when we consider that Quantity is nothing else, but the extension of a thing; and that this extension is expressed by a determinate number of lesser extensions of the same nature; (which lesser ones, are sooner and more easily apprehended then greater; because we are first acquainted and conversant with such; and our understanding graspeth, weigheth and discerneth such more steadily; and maketh an exacter judgment of then;)

* On the Natvre of Bodies (1645), p. 11 *et seq.*

and that such lesser ones are in the greater which they measure, as parts in a whole ; and that the whole by comprehending those parts, is a mere capacity to be divided into them ; we conclude, That *Quantity* or *Bignesse* is nothing else but divisibility ; and that a thing is big, by having a capacity to be divided, or (which is the same) to have parts made of it.

"This is yet more evident (if more may be) in Discrete Quantity (that is, in *number*) then in continued Quantity, or extension. For if we consider any number whatsoever, we shall find the essence of it consisteth in a capacity of being resolved and divided into so many unities, as are contained in it ; which are the parts of it. And this species of Quantity being simpler than the other, serveth for a rule to determine it by : as we may observe in the familiar answers to questions of continued Quantity, which expresse by number the content of it : as when one delivereth the Quantity of a piece of ground, by such a number of furlongs, acres, perches, or the like."

Having thus ascertained, with his customary acuteness, the nature of quantity and two of its species, Digby proceeds to discuss a point which underlies the entire atomic controversy, namely, does quantity consist of parts, or is it one ?

"Ells, feet, inches, are no more reall Entities in the *whole* that is measured by them, and that maketh impressions of such notions in our understanding ; then . . . colour, figure, mel-lownesse, tast, and the like, are several substances in the apple that affecteth our several senses with such various impressions. It is but one *whole*, that may indeed be cut into so many severall parts : but those parts are not really there till by division they are parcelled out : and then the *whole* (out of which they are made) ceaseth to be any longer : and the parts succeed in lieu of it ; and are every one of them a new *whole*.

"This truth is evident out of the very definition we have gathered of Quantity. For since it is *divisibility* (that is, a bare capacity to division) it followeth, that it is not yet divided : and consequently, that those parts are not yet in it which may be made of it ; for division, is the making two or more things of one."

The next step is to point out that if parts be considered to exist in quantity, this must consist of points or indivisibles, "which we shall prove to be impossible." For if quantity were divided into all the parts into which it is divisible, it would be divided into indivisibles ; inasmuch as nothing divisible, and not divided, would remain in it. And as all these parts are actually in quantity, quantity must consist of indivisibles. None of these parts has any necessary claim to be distinguished from the others so as to remain divisible while they become indivisible ;

hence *all* the parts in quantity must be indivisible. But this assertion is encountered by the following dilemma. If indivisibles make quantity, either a finite or infinite number of them must do so. If a finite number, select as an instance three indivisibles, add them together, and make a line (whose extent being only longitude is the first and simplest species of quantity, and therefore whatever is susceptible of partition must be at least a line). Now, by the conditions, this line cannot be divided into more parts than three; yet Euclid (Elements, VI. Prop. 10) has demonstrated that a line can be divided into any number of parts, however great. Therefore it is evident that no line, still less any more complex species of quantity, consists of indivisibles.

Now, Euclid's demonstration being universal, and proving that all extension can be divided infinitely into parts, we must needs confess that it is of the nature of indivisibles, when they coalesce, to be drowned in one another; for otherwise there would result a kind of extension out of them that would be *indivisible*, contrary to the demonstration referred to. But if these indivisibles (even if infinitely numerous) are drowned in one another, they shrink to a single indivisible point. On the other hand, the nature of extension requires that one part be not in the same place where the other is. Therefore quantity cannot consist of an infinite number of indivisibles; and it has been shown that it is not constituted of a finite number. The dilemma terminates; and it is proved that quantity does not consist of indivisibles (*either finite or infinite in number*), and, consequently, that *parts are not actually in it*.

With this answer to a molecular or atomic theorist, it might have been supposed that our acute and critical reasoner would have been content to relinquish the argument. Yet he lingers a little about it to discuss a difficulty, apparently raised by Sense:—Are there not parts in a man's body—for example, arms, legs, fingers, and toes? Digby points out that sense does not judge which is an arm, leg, finger, or toe, but that the notions corresponding to these words are products of the understanding, which, among several functions of a substance, is capable of selecting *one*, as if the substance had no more. We are, therefore, really dealing with a fallacy of confusion. Quantity is a possibility to be made distinct things by division; whereas the different limbs above named "are but a virtue to do distinct things." Even if this were not so, sense cannot determine any one part in a body; for if it could, it would tell precisely where that part begins and ends. If the part begin or end in indivisibles, certainly sense cannot determine of them. On the other hand, considering that all whereof sense is capable is divisible, it continually reminds us of more potential parts than one.

Hence it knows with exactitude neither the One nor the Many.

The special form of fallacy that underlies the atomic theory is the one known as the materialistic. Just as those who assert the existence of matter declare or imply their belief in it as a necessary substratum for hardness, weight, and other properties, which are really their own sensations; so those who advocate the atomic theory, declare or imply their belief in indivisibles, in units of affinity, and so forth, as substrata. On close examination it is found that the substratum referred to has its necessity only in the imagination; and the atomic theory, which has seldom even pretended to adduce experimental evidence for what it affirms to *exist*, is traceable to the same parentage. The same impatience at the recondite nature of forces which we cannot see, which has led many of us to assert so much more than we know, has caused both civilized and savage nations to clothe in statuary their invisible gods. The same impatience, mingled with discontent, is recognizable in that passionate craving for the absolute, or complementary in existence, which is common to mankind. Surrounded on all sides with continuity, motion, and change, our most popular ideas relate to limits, repose, and stability. With the latter, the atomic theory perfectly accords; it readily blends with all the prejudices of our education, and is reinforced by them; so that after some years it becomes an essential part of the mind, which has no longer the power to reject it, even with the aid of the desire. How hard it is, even for a young idealist, to be content with Nature as she is! Such considerations show the subtlety of atomicism, and account for its long and obstinate survival.

One of the most remarkable points in connexion with the history of the atomic theory is the manner in which the actual realization of the atom has been kept in the background. It would be a matter of the highest importance, one would imagine, especially on the part of experimental advocates, to adduce, or at any rate to endeavour to adduce, an atom itself as the best proof of its own existence. Not only has this never been done, but no attempts have been made to do it; and it is probable that the most enthusiastic atomist would be the first to smile at such an effort, or ridicule the supposed discovery. For who has ever seen that which he cannot divide? or who, being unable to divide, would not at once suspect a defect in his tools rather than indivisibility in the substance submitted to experiment? The experience of two thousand years has failed to produce or to discover a single atom of the innumerable millions that have existed during the whole of that time, and still remain unhurt in their modest retirement. Yet, in the present day, they are

spoken of as familiarly as if they were fossils. The ingenuous confession of Gregory is difficult to reconcile with his practice, but it doubtless expresses the feeling of many atomists: "we may admit the atomic theory. It is to be observed, however, that we have no positive proof of its truth, nor are we likely to obtain such proof." Of what use is it to serve a writ of *habeas corpus* upon such a theory?

At this point my mind naturally recurs to a period in the history of chemistry when the science was in one particular respect under as anomalous a régime as prevails at present. From about the year 1700 the belief in *phlogiston* prevailed for three quarters of a century, and was as intimately associated with experimental inquiries as the atom is now; and this belief, as any one who has read a fragment of the literature of that epoch must have observed, was as real and living as can be conceived. Yet, in 1764, Macquer* confesses, "Hitherto chymists have never been able to obtain the phlogiston quite pure and free from every other substance;" and Bishop Watson, in 1800 (1781?), with a somewhat ruffled dignity, exclaims†, "You do not surely expect that chemistry should be able to present you with a handful of phlogiston separated from an inflammable body!" In course of time the nature of phlogiston varied as much as the atomic weight of any modern element. It began with being *materia vel principium ignis, non ipse ignis*, and ended with a narrow escape from identification with hydrogen. It was as material as Lavoisier's *caloric*. Yet chemists argued universally, and apparently by preference, without any quest of the substance itself. How the native freedom of an experimental science could coexist in the same person with so marvellous an abrogation of that freedom was long a puzzling phenomenon to me. The phlogistian, however, is much surpassed by the atomist. The former never ascribed to his veiled companion an attribute without natural analogy; but the latter teaches Tertullian's paradox, *Certum est, quia impossibile*.

When a great system, instead of reposing on clearly ascertained facts, is built upon the sands of fancy, its history must, as a rule, be a record of feeble instability. What has been the case with chemical theory so far as it has been atomic? The absolute, unalterable carbon atom has weighed 6, 3, and 12; that of oxygen was 8 a few years since, now it is 16; but a contemporary chemist proposes to return to the old number. At first the atoms are introduced with radiant rods or lines of attraction; then these appendages appear to have become superfluous, for we hear nothing of them for many years; now they are to be seen on numerous lecture-tables, are treated of in most

* *Traité*, i. p. 10.

† *Essays*, i. p. 167.

systematic works, and it is the object of the majority of chemical researches to develop formulæ in connexion with them. Our modern theorist "explains" the existence of the two bromides ($C^3 H^5 Br$, $C^3 H^5 Br^3$) on the principle of atomicity; while the latter of their two analogues ($I Cl$, $I Cl^3$) is a "molecular combination." This is certainly the most pitiful evasion that ever passed under the name of theory. Again, the hypothesis of specific volumes, which represents a natural fact, is now in a languishing state because we cannot determine how many atoms and how much space make up a given volume of a substance.

It is not difficult to show that the doctrine of atoms involves several important contradictions, in addition to those previously alluded to in this tract. The theory of compound radicals shows conclusively, in its own way, that whatever compound radicals may do, is also done or imitated by absolutely homogeneous atoms; their functions are, in short, the same. Hence by the strict necessity of an inductive logic, as well as by the freedom of our nature, we are driven to deny that the atoms are atoms at all. For if the benzoyl atom ($C^7 H^5 O$) and chlorine atom (Cl) agree in so many of their functions, the probability is that they will agree somewhat in another, namely, complexity. The atomic theorist, however, is too anxious to save himself to allow this conclusion. Reversing history, he takes the chlorine atom first, compares the benzoyl atom with it, and asserts that the radical is a *compound atom*. To have asserted that the atom is a compound radical, would merely have been to narrate the course of a probable discovery; to pronounce the radical a compound atom is to state a pure contradiction, which is, by the laws of language, completely unintelligible.

These are the parts of a system which has been termed, in modern times, an exact science! It is consoling to remember that the most fanciful period of the phlogistic theory immediately preceded the epoch when that theory was extinguished—when chemists, free for the moment from the fetters of a doctrine which called every operation a combustion, perceived the whole of nature to be open to their inquiries. Such a reform and such a liberation are needed, and may be hoped for now.

This memoir would be very incomplete were I to leave unnoticed the opinions of some of the more gifted thinkers with regard to the atomic theory. Newton, for example, is often referred to as an authority on the side of the atomist. That philosopher, indeed, considered it probable that "God, in the beginning, formed matter in solid, massy, hard, impenetrable, moveable particles" which never wear or break to pieces, "no ordinary power being able to divide what God himself made One

in the first creation"*. He also followed Lucretius in asserting that nature would not be lasting were the properties of these particles other than he supposes them to be. It will be observed that Newton allows of indivisibility only so far as ordinary or natural forces are concerned. Elsewhere, in a passage too often overlooked, he limits the indivisibility to his own time. "But whether these parts, distinct and as yet undivided by natural forces, are able to be divided and sundered in their turn is uncertain"†. And again, he allows that "space is divisible *in infinitum*"‡. It appears, then, that Newton had hardly reached so great a degree of decision upon this subject as is commonly believed.

Descartes has also been reckoned among the atomists, probably more from the circumstance that he was a strong systematizer and formalist than on the basis of any of his extant works. That Descartes himself would not have approved of such an imputation is clear from the following (translated) passage§:—"It is also very easy to recognize that there can be in it" (substance) "no atoms, that is to say, parts of bodies or matter which are by nature indivisible, as some philosophers have imagined; inasmuch as, however small we may suppose these parts to be, yet, since they must be extended, we see there is not one of them that cannot be further divided into two or more others of smaller size, and hence is divisible." He then goes on to argue that it would be impossible, at any rate, to restrict the power of the Deity in division; and adds that it is of the nature of even the smallest extended particle in the world to be divisible.

Leibnitz, moreover, has left on record not a few decided expressions of opinion with regard to this subject. Thus he asserts|| that "a material being could not be at the same time material and perfectly indivisible or endowed with real unity" (p. 580). "Material atoms are contrary to reason, besides being still composed of parts; for the invincible attachment of one part to another (if we could reasonably conceive or suppose such a thing) would not destroy their diversity" (p. 584). "Limits are viciously assigned to division and subtleness as well as to the richness and beauty of nature, when atoms and a void, or certain prime elements, including the Cartesian, are set up in the place of true units, when the infinite is not recognized in every thing, and the exact expression of the greatest in the least" (p. 599).

Few among us would deny a hearing to Kant on a question of which philosophy has, from the earliest times, constituted so

* Horsley's Newton, vol. iv. p. 260 *et seq.*

† *Principia*, vol. iii. p. 358 (1713).

‡ Horsley, p. 263.

§ Cousin's Ed. (1824) vol. iii. p. 137. || *Œuvres* (Jacques), vol. i.

large a part. In his 'Observations on the Second Antinomy of Pure Reason'*, where the composition of substance is discussed, the following decisive remarks occur. "These objections" (to the infinite subdivisibility of matter) "lay themselves open at first sight to suspicion, from the fact that they do not recognize the clearest mathematical proofs as propositions relating to the constitution of space, in so far as it is really the formal condition of the possibility of all matter, but regard them merely as inferences from abstract but arbitrary conceptions which cannot have any application to real things. Just as if it were possible to imagine another mode of intuition than that given in the primitive intuition of space; and just as if its *à priori* determinations did not apply to every thing, the existence of which is possible from the fact alone of its filling space. If we listen to them, we shall find ourselves required to cogitate, in addition to the mathematical point, which is simple,—not, however, a part, but a mere limit of space—physical points, which are indeed likewise simple, but possess the peculiar property, as parts of space, of filling it by their aggregation. I shall not repeat here the common and clear refutations of this absurdity which are to be found everywhere in numbers; every one knows that it is impossible to undermine the evidence of mathematics by mere discursive conceptions It is not sufficient to find the conception of the simple for the pure *conception* of the composite, but we must discover for the *intuition* of the composite (matter) the intuition of the simple. Now this, according to the laws of sensibility, and consequently in the case of objects of sense, is utterly impossible."

Davy and Wollaston both refused to accept the atomic theory. Coming still nearer to our own time, I mention, in the last place, a great investigator who has but recently departed from among us. No one could be more acute, and certainly none more clear, than Faraday in the kind of reasoning that precedes discovery. This eminently successful acuteness and clearness were not, however, acquired by the aid of graphic formulæ or wooden models, nor were they accompanied by the doubtful support of any such material assistance. As the air grew thinner, his wing was broadened and its thrust more strong. In 1844, Faraday published† a 'Speculation touching Electric Conduction and the Nature of Matter,' in which the principal subject of discussion is the atomic theory. Starting with the datum, admitted by atomists, that matter consists of atoms and space, he observes that this is "at best an assumption; of the truth of which we can assert nothing, whatever we may say or think of its proba-

* Meiklejohn's Translation of the Kritik, p. 275.

† Phil. Mag. S. 3. vol. xxiv. p. 136.

bility. The word atom, which can never be used without involving much that is purely hypothetical, is often *intended* to be used to express a simple fact; but, good as the intention is, I have not yet found a mind that did habitually separate it from its accompanying temptations; and there can be no doubt that the words definite proportions, equivalents, primes, &c., which did and do express fully all the *facts* of what is usually called the atomic theory in chemistry, were dismissed because they were not expressive enough, and did not say all that was in the mind of him who used the word atom in their stead; they did not express the hypothesis as well as the fact. But it is always safe and philosophic to distinguish, as much as is in our power, fact from theory; and considering the constant tendency of the mind to rest on an assumption, and, when it answers every present purpose, to forget that it is an assumption, we ought to remember that it, in such cases, becomes a prejudice, and inevitably interferes, more or less, with a clear-sighted judgment." Now, of the two constituents of matter, space is the only continuous one. Consider, then, the case of shellac, a non-conductor. Space, in it, must be an insulator, whatever the atoms may be; for if it were a conductor, the shellac could not insulate. But now take the case of platinum, which must also be composed of atoms and space. Since platinum is a conductor, space, being its only continuous constituent, must be a conductor. Space, which is everywhere uniform, is therefore a conductor and a non-conductor. "Any ground of reasoning which tends to such conclusions as these must in itself be false." The facts do not warrant any other conclusion than that what we call matter is *continuous*. Indeed "a mind just entering on the subject may consider it difficult to think of the powers of matter independent of a separate something to be called *the matter*; but it is certainly far more difficult, and indeed impossible, to think of or imagine that *matter* independent of the powers. Now the powers we know and recognize in every phenomenon of the creation, the abstract matter in none; why then assume the existence of that of which we are ignorant, which we cannot conceive, and for which there is no philosophical necessity?"

If we must assume at all, let us assume as little as possible. The system of Boscovich is in these respects superior to the atomic; it assumes much less, and does not contradict the facts of nature. In it Matter and the atom disappear; and we find that substances are constituted of centres of force, attractive and repulsive. For the *shape* of the atom, the direction and relative intensity of these individual forces are substituted. "Matter is not merely mutually penetrable, but each atom" (centre) "extends, so to say, throughout the whole of the solar system, yet always retaining its own centre of force."

Here Faraday proclaims himself at once a Leibnitzian and idealist. No answer, so far as I am aware, has ever been made to his argument; nor did he, in the exuberant development of atomic suggestions which surrounded his later years, publish any retraction of his previous opinion. Therefore, that matter is *force, in some way determined*, was probably that great thinker's final belief.

Such being the condition of the atomic theory, whether regarded in its chemical or philosophical aspect, certain practical results follow. I shall not take into consideration the physical molecules, which are "invested with an arbitrary system of central forces invented expressly to account for the observed phenomena," and are hard—nor the new alternative of ring-vortices, which are not hard*. A logical mind, still free to make an effort, cannot be content to accept that theory without question, or to entertain it without suspicion. And on inquiry it will find, if my argument be sound, that the atomic theory has no experimental basis, is untrue to nature generally, and consists in the main of a materialistic fallacy, derived from appetite more than from judgment; while, on the other side, arises the IDEA or MOTION, with its subordinate laws, true both to nature and the life of man, the highest product of the scientific and the pure reason, and the noblest generalization the world has yet known, because it is the only one that neither limits nor enslaves. So serious is your crisis, so momentous your decision.

12 Pemberton Terrace,
St. John's Park, N.

Section VI

THE PROBLEMS ARE RESOLVED

William Thomson, later Lord Kelvin, was one of the outstanding physicists and engineers of the nineteenth century, who took a great interest in theories of matter. This address is typical of his approach; the French philosopher Pierre Duhem considered that British scientists, of whom he took Thomson as the example, had 'ample' minds, and reasoned by analogy from mechanical models; whereas Frenchmen had 'deep' mathematical minds. Thomson had been one of those responsible for the acceptance of the kinetic theory of heat. He had reservations about the kinetic theory of gases—because of the principle of equipartition of energy—but his point in this address is that in the theory elastic particles are taken for granted. Yet it should be possible to give some explanation of the elasticity of the particles, since otherwise the elasticity of gases was not really explained at all. So he tried flywheel systems, and fluid circulations through apertures, as models having elasticity as a matter of course rather than inexplicably built in. Finally, he pointed to his own vortex atom, in which the particles were conceived to be aethereal smoke rings which, since the aether was a perfect, frictionless fluid, would never come to a standstill and would be highly elastic.

William Crookes' address is famous for the theory of inorganic evolution which it contains. Darwin's *Origin of Species* had appeared in 1859, and by the 1880s the theory of biological evolution was generally accepted. Crookes sought to show the parallels between the chemical elements, as arranged in families in Mendeléeff's Periodic Table, and the genera and species of biology. The surprising fauna of Australia has its inorganic analogue in the Rare Earth metals of Sweden, a group of elements on which Crookes had been working. To account for their very close similarities in properties, he proposed that they were mere 'meta-elements'. The atoms of any given element were not all exactly alike, some being heavier than the mean, and some lighter. In the Rare Earths complete separation into elements had not taken place, and one found a mixture of atoms having a range of weights. Until after the work of Moseley and Niels Bohr in the second decade of the twentieth century, it was impossible to tell how many Rare Earth elements there were. Crookes' 'meta-elements' look like ancestors of our 'isotopes', but much more speculative in origin.

Wilhelm Ostwald represents the last attempt to divert attention away from atoms. He advocated instead a chemistry based on dynamics, or the study of energy changes, employing the laws of thermodynamics. Ostwald was also one of the last chemists to claim that hypotheses derived from physics should be excluded from chemistry. In a tradition going back to the *Naturphilosophie* of a century earlier—represented here by Davy, Faraday, Carey Foster, and Mills—he saw matter merely as a complex of energies which we find together in the same place. From the Phase Rule, governing the behaviour of alloys and solutions, Ostwald claimed that one could derive the laws of chemical combination without introducing hypotheses; and even account for isomerism, although he did not do so.

Ostwald's remarks produced some consternation among chemists, but physicists, busily studying atomic disintegration, took no notice. Then Einstein investigated the Brownian Motion and showed that it could be accounted for in terms of molecular movement. Jean Perrin also made extensive studies of the Brownian Motion, and in his long paper, which appeared in English (translated by Frederick Soddy) in the form of a book, finally made the question of whether atoms existed no longer interesting for chemists. Attention now shifted to the nature and status of the sub-atomic particles, the way the Periodic Table was constructed, and the explanation of chemical affinity in terms of the protons and electrons of the physicists' atomic theory. The introductory part only of Perrin's paper has been reprinted here.

FURTHER READING

- P. Duhem, *The Aim and Structure of Physical Theory*, trans. P. P. Wiener, Princeton, 1954, pt. I, chap. 5
R. H. Silliman, 'William Thomson: Smoke Rings and Nineteenth Century Atomism', *Isis*, LIV (1963), 461-74
M. W. Travers, *A Life of Sir William Ramsay*, London, 1956, chap. 17
S. Wright (ed.), *Classical Scientific Papers, Physics*, London, 1964

TRANSACTIONS OF THE SECTIONS.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCE.

PRESIDENT OF THE SECTION—

Professor Sir WILLIAM THOMSON, M.A., LL.D., D.C.L., F.R.S.L. & E., F.R.A.S.

THURSDAY, AUGUST 28.

The PRESIDENT delivered the following Address:—

Steps towards a Kinetic Theory of Matter.

THE now well-known kinetic theory of gases is a step so important in the way of explaining seemingly static properties of matter by motion, that it is scarcely possible to help anticipating in idea the arrival at a complete theory of matter, in which all its properties will be seen to be merely attributes of motion. If we are to look for the origin of this idea, we must go back to Democritus Epicurus and Lucretius. We may then, I believe, without missing a single step, skip 1,800 years. Early last century we find in Malebranche's '*Recherche de la Vérité*,' the statement that '*La dureté des corps*' depends on '*petits tourbillons*.'¹ These words, embedded in a hopeless mass of unintelligible statements of the physical, metaphysical, and theological philosophies of the day, and unsupported by any explanation, elucidation, or illustration throughout the rest of the three volumes, and only marred by any other single sentence or word to be found in the great book, still do express a distinct conception, which forms a most remarkable step towards the kinetic theory of matter. A little later we have Daniel Bernoulli's promulgation of what we now accept as a surest article of scientific faith—the kinetic theory of gases. He, so far as I know, thought only of the Boyle's and Marriot's law of the 'spring of air,' as Boyle called it, without reference to change of temperature or the augmentation of its pressure if not allowed to expand for elevation of temperature, a phenomenon which perhaps he scarcely knew, still less the elevation of temperature produced by compression, and the lowering of temperature by dilatation, and the consequent necessity of waiting for a fraction of a second or a few seconds of time (with apparatus of ordinary experimental magnitude), to see a subsidence from a larger change of pressure, down to the amount of change that verifies Boyle's law. The consideration of these phenomena forty years ago by Joule, in connection with Bernoulli's original conception, formed the foundation of the kinetic theory of gases as we now have it. But what a splendid and useful building has been placed on this foundation by Clausius and Maxwell, and what a beautiful ornament we see on the top of it in the radiometer of Crookes, securely attached to it

¹ 'Preuve de la supposition que j'ay faite: Que la matière subtile ou éthérée est nécessairement composée de PETITS TOURBILLONS; et qu'ils sont les causes naturelles de tous les changements qui arrivent à la matière; ce que je confirme par l'explication des effets les plus généraux de la Physique, tels que sont la dureté des corps, leur fluidité, leur pesanteur, leur légèreté, la lumière et la réfraction et réflexion de ses rayons.'—Malebranche, *Recherche de la Vérité*, 1712.

by the happy discovery of Tait and Dewar,¹ that the length of the free path of the residual molecules of air in a good modern vacuum may amount to several inches. Clausius' and Maxwell's explanations of the diffusion of gases, and of thermal conduction in gases, their charmingly intelligible conclusion that in gases the diffusion of heat is just a little more rapid than the diffusion of molecules, because of the interchange of energy in collisions between molecules,² while the chief transference of heat is by actual transport of the molecules themselves; and Maxwell's explanation of the viscosity of gases, with the absolute numerical relations which the work of those two great discoverers found among the three properties of diffusion, thermal conduction, and viscosity; have annexed to the domain of science a vast and ever-growing province.

Rich as it is in practical results, the kinetic theory of gases, as hitherto developed, stops absolutely short at the atom or molecule, and gives not even a suggestion towards explaining the properties in virtue of which the atoms or molecules mutually influence one another. For some guidance towards a deeper and more comprehensive theory of matter, we may look back with advantage to the end of last century and the beginning of this century, and find Rumford's conclusion regarding the heat generated in boring a brass gun: 'It appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in these experiments, except it be motion,' and Davy's still more suggestive statement: 'The phenomena of repulsion are not dependent on a peculiar elastic fluid for their existence. . . . 'Heat may be defined a peculiar motion, probably a vibration, of the corpuscles of bodies, tending to separate them. . . . 'To distinguish this motion from others, and to signify the causes of our sensations of heat, &c., the name *repulsive* motion has been adopted.' Here we have a most important idea. It would be somewhat a bold figure of speech to say the earth and moon are kept apart by a repulsive motion; and yet, after all, what is centrifugal force but a repulsive motion, and may it not be that there is no such thing as repulsion, and that it is solely by inertia that what seems to be repulsion is produced? Two bodies fly together, and, accelerated by mutual attraction, if they do not precisely hit one another, they cannot but separate in virtue of the inertia of their masses. So, after dashing past one another in sharply concave curves round their common centre of gravity, they fly asunder again. A careless onlooker might imagine they had repelled one another, and might not notice the difference between what he actually sees and what he would see if the two bodies had been projected with great velocity towards one another, and either colliding and rebounding, or repelling one another into sharply convex continuous curves, fly asunder again.

Joule, Clausius, and Maxwell, and no doubt Daniel Bernoulli himself, and I believe every one who has hitherto written or done anything very explicit in the kinetic theory of gases, has taken the mutual action of molecules in collision as repulsive. May it not after all be attractive? This idea has never left my mind

¹ *Proc. R. S. E.* March 2, 1874, and July 5, 1875.

² On the other hand in liquids, on account of the crowdedness of the molecules, the diffusion of heat must be chiefly by interchange of energies between the molecules, and should be, as experiment proves it is, enormously more rapid than the diffusion of the molecules themselves, and this again ought to be much less rapid than either the material or thermal diffusivities of gases. Thus the diffusivity of common salt through water was found by Fick to be as small as '0000112 square centimetres per second: nearly 200 times as great as this is the diffusivity of heat through water, which was found by J. T. Bottomley to be about '002 square centimetres per second. The material diffusivities of gases, according to Loschmidt's experiments, range from '098 (the interdiffusivity of carbonic acid and nitrous oxide) to '642 (the interdiffusivity of carbonic oxide and hydrogen); while the thermal diffusivities of gases, calculated according to Clausius' and Maxwell's kinetic theory of gases, are '089 for carbonic acid, '16 for common air or other gases of nearly the same density, and 1·12 for hydrogen (all, both material and thermal, being reckoned in square centimetres per second).

since I first read Davy's 'Repulsive Motion,' about thirty-five years ago, but I never made anything of it, at all events have not done so until to-day (June 16, 1884), (if this can be said to be making anything of it), when in endeavouring to prepare the present address I notice that Joule's and my own old experiments¹ on the thermal effect of gases expanding from a high pressure vessel through a porous plug, proves the less dense gas to have greater intrinsic *potential* energy than the denser gas, if we assume the ordinary hypothesis regarding the temperature of a gas, according to which two gases are of equal temperatures² when the kinetic energies of their constituent molecules are of equal average amounts per molecule.

Think of the thing thus. Imagine a great multitude of particles enclosed by a boundary which may be pushed inwards in any part all round at pleasure. Now station an engineer corps of Maxwell's army of sorting demons all round the enclosure, with orders to push in the boundary diligently everywhere, when none of the besieged troops are near, and to do nothing when any of them are seen approaching, and until after they have turned again inwards. The result will be that with exactly the same sum of kinetic and potential energies of the same enclosed multitude of particles, the throng has been caused to be denser. Now Joule's and my own old experiments on the efflux of air prove that if the crowd be common air, or oxygen, or nitrogen, or carbonic acid, the temperature is a little higher in the denser than in the rarer condition when the energies are the same. By the hypothesis, equality of temperature between two different gases or two portions of the same gas at different densities means equality of kinetic energies in the same number of molecules of the two. From our observations proving the temperature to be higher, it therefore follows that the potential energy is smaller in the condensed crowd. This—always, however, under protest as to the temperature hypothesis—proves some degree of attraction among the molecules, but it does not prove ultimate attraction between two molecules in collision, or at distances much less than the average mutual distance of nearest neighbours in the multitude. The collisional force might be repulsive, as generally supposed hitherto, and yet attraction might predominate in the whole reckoning of difference between the intrinsic potential energies of the more dense and less dense multitudes. It is, however, remarkable that the explanation of the propagation of sound through gases, and even of the positive fluid pressure of a gas against the sides of the containing vessel, according to the kinetic theory of gases, is quite independent of the question whether the ultimate collisional force is attractive or repulsive. Of course it must be understood that if it is attractive, the particles must be so small that they hardly ever meet—they would have to be infinitely small to *never* meet—that, in fact, they meet so seldom, in comparison with the number of times their courses are turned through large angles by attraction, that the influence of these purely attractive collisions is preponderant over that of the comparatively very rare impacts from actual contact. Thus, after all, the train of speculation suggested by Davy's 'Repulsive Motion' does not allow us to escape from the idea of true repulsion, does not do more than let us say it is of no consequence, nor even say this with truth, because, if there are impacts at all, the nature of the force during the impact, and the effects of the mutual impacts, however rare, cannot be evaded in any attempt to realise a conception of the kinetic theory of gases. And in fact, unless we are satisfied to imagine the atoms of a gas as mathematical points endowed with inertia, and,

¹ Republished in Sir W. Thomson's *Mathematical and Physical Papers*, Vol. I. Article XLIX. p. 381.

² That this is a mere hypothesis has been scarcely remarked by the founders themselves, nor by almost any writer on the kinetic theory of gases. No one has yet examined the question: what is the condition as regards average distribution of kinetic energy, which is ultimately fulfilled by two portions of gaseous matter, separated by a thin elastic septum which absolutely prevents interdiffusion of matter, while it allows interchange of kinetic energy by collisions against itself? Indeed I do not know but that the present is the very first statement which has ever been published of this condition of the problem of equal temperatures between two gaseous masses.

as according to Boscovich, endowed with forces of mutual positive and negative attraction, varying according to some definite function of the distance, we cannot avoid the question of impacts, and of vibrations and rotations of the molecules resulting from impacts, and we must look distinctly on each molecule as being either a little elastic solid, or a configuration of motion in a continuous all-pervading liquid. I do not myself see how we can ever permanently rest anywhere short of this last view; but it would be a very pleasant temporary resting-place on the way to it, if we could, as it were, make a mechanical model of a gas out of little pieces of round perfectly elastic solid matter, flying about through the space occupied by the gas, and colliding with one another and against the sides of the containing vessel. This is, in fact, all we have of the kinetic theory of gases up to the present time, and this has done for us, in the hands of Clausius and Maxwell, the great things which constitute our first step towards a molecular theory of matter. Of course from it we should have to go on to find an explanation of the elasticity and all the other properties of the molecules themselves, a subject vastly more complex and difficult than the gaseous properties, for the explanation of which we assume the elastic molecule; but without any explanation of the properties of the molecule itself, with merely the assumption that the molecule has the requisite properties, we might rest happy for awhile in the contemplation of the kinetic theory of gases, and its explanation of the gaseous properties, which is not only stupendously important as a step towards a more thorough-going theory of matter, but is undoubtedly the expression of a perfectly intelligible and definite set of facts in nature. But alas for our mechanical model consisting of the cloud of little elastic solids flying about amongst one another. Though each particle have absolutely perfect elasticity, the end must be pretty much the same as if it were but imperfectly elastic. The average effect of repeated and repeated mutual collisions must be to gradually convert all the translational energy into energy of shriller and shriller vibrations of the molecule. It seems certain that each collision must have something more of energy in vibrations of very finely divided nodal parts than there was of energy of such vibrations before the impact. The more minute this nodal subdivision, the less must be the tendency to give up part of the vibrational energy into the shape of translational energy in the course of a collision, and I think it is rigorously demonstrable that the whole translational energy must ultimately become transformed into vibrational energy of higher and higher nodal subdivisions if each molecule is a continuous elastic solid. Let us, then, leave the kinetic theory of gases for a time with this difficulty unsolved, in the hope that we or others after us may return to it, armed with more knowledge of the properties of matter, and with sharper mathematical weapons to cut through the barrier which at present hides from us any view of the molecule itself, and of the effects other than mere change of translational motion which it experiences in collision.

To explain the elasticity of a gas was the primary object of the kinetic theory of gases. This object is only attainable by the assumption of an elasticity more complex in character, and more difficult of explanation, than the elasticity of gases—the elasticity of a solid. Thus, even if the fatal fault in the theory, to which I have alluded, did not exist, and if we could be perfectly satisfied with the kinetic theory of gases founded on the collisions of elastic solid molecules, there would still be beyond it a grander theory which need not be considered a chimerical object of scientific ambition—to explain the elasticity of solids. But we may be stopped when we commence to look in the direction of such a theory with the cynical question: What do you mean by explaining a property of matter? As to being stopped by any such question, all I can say is that if engineering were to be all and to end all physical science, we should perforce be content with merely finding properties of matter by observation, and using them for practical purposes. But I am sure very few, if any, engineers are practically satisfied with so narrow a view of their noble profession. They must and do patiently observe, and discover by observation, properties of matter, and results of material combinations. But deeper questions are always present, and always fraught with interest to the true engineer, and he will be the last to give weight to any other objection to any attempt to see below the surface of things than the practical question: Is it likely

to prove wholly futile? But now, instead of imagining the question: What do you mean by explaining a property of matter? to be put cynically, and letting ourselves be irritated by it, suppose we give to the questioner credit for being sympathetic, and condescend to try and answer his question. We find it not very easy to do so. All the properties of matter are so connected that we can scarcely imagine one *thoroughly explained* without our seeing its relation to all the others, without in fact having the explanation of all; and till we have this we cannot tell what we mean by 'explaining a property,' or 'explaining the properties' of matter. But though this consummation may never be reached by man, the progress of science may be, I believe will be, step by step towards it, on many different roads converging towards it from all sides. The kinetic theory of gases is, as I have said, a true step on one of the roads. On the very distinct road of chemical science, St. Clair Deville arrived at his grand theory of dissociation without the slightest aid from the kinetic theory of gases. The fact that he worked it out solely from chemical observation and experiment, and expounded it to the world without any hypothesis whatever, and seemingly even without consciousness of the beautiful explanation it has in the kinetic theory of gases, secured for it immediately an independent solidity and importance as a chemical theory when he first promulgated it, to which it might even by this time scarcely have attained if it had first been suggested as a probability indicated by the kinetic theory of gases, and been only afterwards confirmed by observation. Now, however, guided by the views which Clausius and Williamson have given us of the continuous interchange of partners between the compound molecules constituting chemical compounds in the gaseous state, we see in Deville's theory of dissociation a point of contact of the most transcendent interest between the chemical and physical lines of scientific progress.

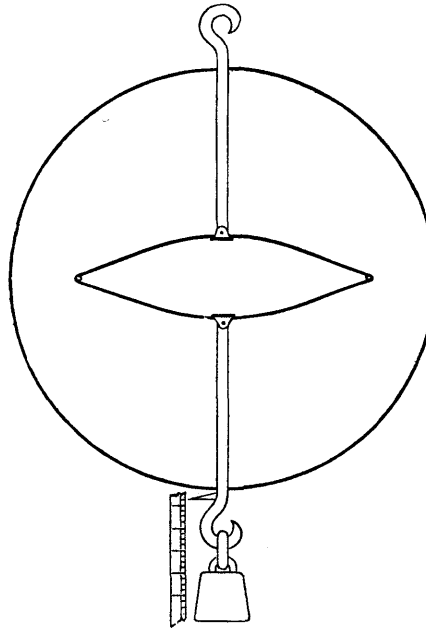
To return to elasticity: if we could make out of matter devoid of elasticity a combined system of relatively moving parts which, in virtue of motion, has the essential characteristics of an elastic body, this would surely be, if not positively a step in the kinetic theory of matter, at least a finger-post pointing a way which we may hope will lead to a kinetic theory of matter. Now this, as I have already shown,¹ we can do in several ways. In the case of the last of the communications referred to, of which only the title has hitherto been published, I showed that, from the mathematical investigation of a gyrostatically dominated combination contained in the passage of Thomson and Tait's 'Natural Philosophy' referred to, it follows that any ideal system of material particles, acting on one another mutually through massless connecting springs, may be perfectly imitated in a model consisting of rigid links jointed together, and having rapidly rotating fly-wheels pivoted on some or on all of the links. The imitation is not confined to cases of equilibrium. It holds also for vibration produced by disturbing the system infinitesimally from a position of stable equilibrium and leaving it to itself. Thus we may make a gyrostatic system such that it is in equilibrium under the influence of certain positive forces applied to different points of this system; all the forces being precisely the same as, and the points of application similarly situated to, those of the stable system with springs. Then, provided proper masses (that is to say, proper amounts and distributions of inertia) be attributed to the links, we may remove the external forces from each system, and the consequent vibration of the points of application of the forces will be identical. Or we may act upon the systems of material points and springs with any given forces for any given time, and leave it to itself, and do the same thing for the gyrostatic system; the consequent motion will be the same in the two cases. If in the one case the springs are made more and more stiff, and in the other case the angular velocities of the fly-wheels are made greater and greater, the periods of the vibrational constituents of

¹ Paper on 'Vortex Atoms,' *Proc. R. S. E.* Feb. 1867; abstract of Lecture before Royal Institution of Great Britain, March 4, 1881, on 'Elasticity viewed as possibly a Mode of Motion;' Thomson and Tait's *Natural Philosophy*, second edition, Part I. §§ 345 viii to 345 xxvii; 'On Oscillation and Waves in an Adynamic Gyrostatic System' (title only), *Proc. R. S. E.* March 1883.

the motion will become shorter and shorter, and the amplitudes smaller and smaller, and the motions will approach more and more nearly those of two perfectly rigid groups of material points, moving through space and rotating according to the well-known mode of rotation of a rigid body having unequal moments of inertia about its three principal axes. In one case the ideal nearly rigid connection between the particles is produced by massless exceedingly stiff springs; in the other case it is produced by the exceedingly rapid rotation of the fly-wheels in a system which, when the fly-wheels are deprived of their rotation, is perfectly limp.

The drawings (Figs. 1 and 2) before you illustrate two such material systems.¹ The directions of rotation of the fly-wheels in the gyrostatic system (fig. 2) are indicated by directional ellipses, which show in perspective the direction of rotation of the fly-wheel of each gyrostat. The gyrostatic system (fig. 2) might have been constituted of two gyrostatic members, but four are shown for symmetry. The enclosing circle represents in each case in section an enclosing spherical shell to

FIG. 1.



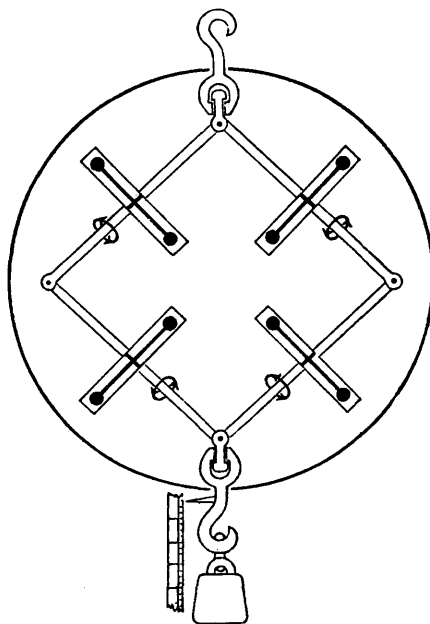
prevent the interior from being seen. In the inside of one there are fly-wheels, in the inside of the other a massless spring. The projecting hooked rods seem as if they are connected by a spring in each case. If we hang any one of the systems up by the hook on one of its projecting rods, and hang a weight to the hook of the other projecting rod, the weight when first put on will oscillate up and down, and will go on doing so for ever if the system be absolutely unfrictional. If we check

¹ In fig. 1 the two hooked rods seen projecting from the sphere are connected by an elastic coach spring. In fig. 2 the hooked rods are connected one to each of two opposite corners of a four-sided jointed frame, each member of which carries a gyrostat so that the axis of rotation of the fly-wheel is in the axis of the member of the frame which bears it. Each of the hooked rods in fig. 2 is connected to the framework through a swivel joint, so that the whole gyrostatic framework may be rotated about the axis of the hooked rods in order to annul the moment of momentum of the framework about this axis due to rotation of the fly-wheels in the gyrostats.

the vibration by hand, the weight will hang down at rest, the pin drawn out to a certain degree; and the distance drawn out will be simply proportional to the weight hung on, as in an ordinary spring balance.

Here, then, out of matter possessing rigidity, but absolutely devoid of elasticity, we have made a perfect model of a spring in the form of a spring balance. Connect millions of millions of particles by pairs of rods such as these of this spring balance, and we have a group of particles constituting an elastic solid; exactly fulfilling the mathematical ideal worked out by Navier, Poisson, and Cauchy, and many other mathematicians who, following their example, have endeavoured to found a theory of the elasticity of solids on mutual attraction and repulsion between a group of material particles. All that can possibly be done by this theory, with its assumption of forces acting according to any assumed law of relation to distance, is done by the gyrostatic system. But the gyrostatic system does, besides, what

FIG. 2.



the system of naturally acting material particles cannot do: it constitutes an elastic solid which can have the Faraday magneto-optic rotation of the plane of polarisation of light; supposing the application of our solid to be a model of the luminiferous ether for illustrating the undulatory theory of light. The gyrostatic model spring balance is arranged to have zero moment of momentum as a whole, and therefore to contribute nothing to the Faraday rotation; with this arrangement the model illustrates the luminiferous ether in a field unaffected by magnetic force. But now let there be a different rotational velocity imparted to the jointed square round the axis of the two projecting hooked rods, such as to give a resultant moment of momentum round any given line through the centre of inertia of the system, and let pairs of the hooked rods in the model thus altered, which is no longer a model of a mere spring-balance, be applied as connections between millions of pairs of particles as before: with the lines of resultant moment of momentum all similarly directed. We now have a model elastic solid which will have the property that the direction of vibration in waves of rectilinear vibrations propagated through

it shall turn round the line of propagation of the waves; just as Faraday's observation proves to be done by the line of vibration of light in a dense medium between the poles of a powerful magnet. The case of wave front perpendicular to the lines of resultant moment of momentum (that is to say, the direction of propagation being parallel to these lines) corresponds, in our mechanical model, to the case of light travelling in the direction of the lines of force in a magnetic field.

In these illustrations and models we have different portions of ideal rigid matter acting upon one another, by normal pressure at mathematical points of contact—of course no forces of friction are supposed. It is exceedingly interesting to see how thus, with no other postulates than inertia, rigidity, and mutual impenetrability, we can thoroughly model not only an elastic solid, and any combination of elastic solids, but so complex and recondite a phenomenon as the passage of polarized light through a magnetic field. But now, with the view of ultimately discarding the postulate of rigidity from all our materials, let us suppose some to be absolutely destitute of rigidity, and to possess merely inertia and incompressibility, and mutual impenetrability with reference to the still remaining rigid matter. With these postulates we can produce a perfect model of mutual action at a distance between solid particles, fulfilling the condition, so keenly desired by Newton and Faraday, of being explained by continuous action through an intervening medium. The law of the mutual force in our model, however, is not the simple Newtonian law, but the much more complex law of the mutual action between two electromagnets—with this difference, that in the hydrokinetic model in every case the force is opposite in direction to the corresponding force in the electromagnetic analogue. Imagine a solid bored through with a hole and placed in our ideal perfect liquid. For a moment let the hole be stopped by a diaphragm, and let an impulsive pressure be applied for an instant uniformly over the whole membrane, and then instantly let the membrane be dissolved into liquid. This action originates a motion of the liquid relatively to the solid, of a kind to which I have given the name of 'irrotational circulation,' which remains absolutely constant however the solid be moved through the liquid. Thus, at any time the actual motion of the liquid at any point in the neighbourhood of the solid will be the resultant of the motion it would have in virtue of the circulation alone, were the solid at rest, and the motion it would have in virtue of the motion of the solid itself, had there been no circulation established through the aperture. It is interesting and important to remark in passing that the whole kinetic energy of the liquid is the sum of the kinetic energies which it would have in the two cases separately. Now, imagine the whole liquid to be enclosed in an infinitely large rigid containing vessel, and in the liquid, at an infinite distance from any part of the containing vessel, let two perforated solids, with irrotational circulation through each, be placed at rest near one another. The resultant fluid motion due to the two circulations will give rise to fluid pressure on the two bodies, which if unbalanced will cause them to move. The force systems—force-and-torques, or pairs of forces—required to prevent them from moving will be mutual and opposite, and will be the same as, but opposite in direction to, the mutual force systems required to hold at rest two electromagnets fulfilling the following specification. The two electromagnets are to be of the same shape and size as the two bodies, and to be placed in the same relative positions, and to consist of infinitely thin layers of electric currents in the surfaces of solids possessing extreme diamagnetic quality—in other words, infinitely small permeability. The distribution of electric current on each body may be any whatever which fulfils the condition that the total current across any closed line drawn on the surface once through the aperture is equal to $1/4\pi$ of the circulation¹ through the aperture in the hydrokinetic analogue.

It might be imagined that the action at a distance thus provided for by fluid motion could serve as a foundation for a theory of the equilibrium, and the

¹ The integral of tangential component velocity all round any closed curve, passing once through the aperture, is defined as the 'Cyclic constant,' or the 'circulation' ('Vortex Motion,' § 60 (a), *Trans. R. S. E.* April 29, 1867). It has the same value for all closed curves passing just once through the aperture, and it remains constant through all time whether the solid body be in motion or at rest.

vibrations, of elastic solids, and the transmission of waves like those of light through an extended quasi-elastic solid medium. But unfortunately for this idea the equilibrium is essentially unstable, both in the case of magnets and, notwithstanding the fact that the forces are oppositely directed, in the hydrokinetic analogue also, when the several movable bodies (two or any greater number) are so placed relatively as to be in equilibrium. If, however, we connect the perforated bodies with circulation through them in the hydrokinetic system, by jointed rigid connecting links, we may arrange for configurations of stable equilibrium. Thus without fly-wheels, but with fluid circulations through apertures, we may make a model spring balance, or a model luminiferous ether, either without or with the rotational quality corresponding to that of the true luminiferous ether in the magnetic fluid—in short, do all by the perforated solids with circulations through them that we saw we could do by means of linked gyrostats. But something that we cannot do by linked gyrostats we can do by the perforated bodies with fluid circulation. We can make a model gas. The mutual action at a distance, repulsive or attractive according to the mutual aspect of the two bodies when passing within collisional distance ¹ of one another, suffices to produce the change of direction of motion in collision, which essentially constitutes the foundation of the kinetic theory of gases; and which, as we have seen before, may as well be due to attraction as to repulsion, so far as we know from any investigation hitherto made in this theory.

There remains, however, as we have seen before, the difficulty of providing for the case of actual impacts between the solids; which must be done by giving them massless spring buffers, or, which amounts to the same thing, attributing to them repulsive forces sufficiently powerful at very short distances to absolutely prevent impacts between solid and solid; unless we adopt the equally repugnant idea of infinitely small perforated solids, with infinitely great fluid circulations through them. Were it not for this fundamental difficulty, the hydrokinetic model gas would be exceedingly interesting; and, though we could scarcely adopt it as conceivably a true representation of what gases really are, it might still have some importance as a model configuration of solid and liquid matter, by which without elasticity the elasticity of a true gas might be represented.

But lastly, since the hydrokinetic model gas with perforated solids and fluid circulations through them fails because of the impacts between the solids, let us annul the solids and leave the liquid performing irrotational circulation round vacancy,² in the place of the solid cores which we have hitherto supposed; or let us annul the rigidity of the solid cores of the rings and give them molecular rotation according to Helmholtz's theory of vortex motion. For stability the molecular rotation must be such as to give the same velocity at the boundary of the rotational fluid core as that of the irrotationally circulating liquid in contact with it, because, as I have proved, frictional slip between two portions of liquid in contact is inconsistent with stability. There is a further condition, upon which I cannot enter in detail just now, but which may be understood in a general way when I say that it is a condition of either uniform or of increasing molecular rotation from the surface inwards, analogous to the condition that the density of a liquid, resting for example under the influence of gravity, must either be uniform or must be greater below than above for stability of

¹ According to this view there is no precise distance, or definite condition respecting the distance, between two molecules at which apparently they come to be in collision, or when receding from one another they cease to be in collision. It is convenient, however, in the kinetic theory of gases, to adopt arbitrarily a precise definition of collision, according to which two bodies or particles mutually acting at a distance may be said to be in collision when their mutual action exceeds some definite arbitrarily assigned limit, as, for example, when the radius of curvature of the path of either body is less than a stated fraction (1/100, for instance) of the distance between them.

² Investigations respecting coreless vortices will be found in a paper by the author, 'Vibrations of a Columnar Vortex,' *Proc. R. S. E.* March 1, 1880; and a paper by Hicks, recently read before the Royal Society.

equilibrium. All that I have said in favour of the model vortex gas composed of perforated solids with fluid circulations through them holds without modification for the purely hydrokinetic model, composed either of Helmholtz cored vortex rings or of coreless vortices, and we are now troubled with no such difficulty as that of the impacts between solids. Whether, however, when the vortex theory of gases is thoroughly worked out, it will or will not be found to fail in a manner analogous to the failure which I have already pointed out in connection with the kinetic theory of gases composed of little elastic solid molecules, I cannot at present undertake to speak with certainty. It seems to me most probable that the vortex theory cannot fail in any such way, because all I have been able to find out hitherto regarding the vibration of vortices,¹ whether cored or coreless, does not seem to imply the liability of translational or impulsive energies of the individual vortices becoming lost in energy of smaller and smaller vibrations.

As a step towards kinetic theory of matter it is certainly most interesting to remark that in the quasi-elasticity, elasticity looking like that of an india-rubber band, which we see in a vibrating smoke-ring launched from an elliptic aperture, or in two smoke-rings which were circular, but which have become deformed from circularity by mutual collision, we have in reality a virtual elasticity in matter devoid of elasticity, and even devoid of rigidity, the virtual elasticity being due to motion, and generated by the generation of motion.

SECTION B.—CHEMICAL SCIENCE.

PRESIDENT OF THE SECTION—WILLIAM CROOKES, F.R.S., V.P.C.S.

THURSDAY, SEPTEMBER 2.

The PRESIDENT delivered the following Address:—

A GLANCE over the Presidential Addresses delivered before this Section on former occasions will show that the occupiers of this chair have ranged over a fairly wide field. Some of my predecessors have given a general survey of the progress of chemical science during the past year; some, taking up a technological aspect of the subject, have discussed the bearings of chemistry upon our national industries; others, again, have passed in review the various institutions in this country for teaching chemistry; and in yet other cases the speaker has had the opportunity of bringing before the scientific world, for the first time, an account of some important original researches.

On this occasion I venture to ask your attention to a few thoughts on the very foundations of chemistry as a science—on the nature and the probable, or at least possible, origin of the so-called elements. If the views to which I have been led may at first glance appear heretical, I must remind you that in some respects they are shared more or less, as I shall subsequently show, by not a few of the most eminent authorities, and notably by one of my predecessors in this chair, Dr. J. H. Gladstone, F.R.S., to whose brilliant address, delivered in 1883, I must beg to refer you.

Should it not sometimes strike us, chemists of the present day, that after all we are in a position unpleasantly akin to that of our forerunners, the alchemists of the Middle Ages? These necromancers of a time long past did not, indeed, draw so sharp a line as do we between bodies simple and compound; yet their life-task was devoted to the formation of new combinations, and to the attempt to transmute bodies which we commonly consider as simple and ultimate—that is, the metals. In the department of synthesis they achieved very considerable successes; in the transmutation of metals their failure is a matter of history.

But what are we of this so-called Nineteenth Century doing in our laboratories and our libraries? Too many of us are content to acquire simply what others have already observed and discovered, with an eye directed mainly to medals, certificates, diplomas, and other honours recognised as the fruits of 'passing.' Others are seeking to turn the determined facts of chemistry to useful purposes; whilst a third class, sometimes not easily distinguished from the second, are daily educing novel organic compounds, or are racking their ingenuity to prepare artificially some product which Nature has hitherto furnished us through the instrumentality of plants and animals. The practical importance of such investigations, and their bearing on the industrial arts and on the purposes and needs of daily life, have been signally manifested during the last half-century.

Still a fourth class of inquirers, working at the very confines of our knowledge, find themselves occasionally at least face to face with a barrier which has hitherto proved impassable, but which must be overthrown, surmounted, or turned, if chemical science is ever to develop into a definite, an organised unity. This barrier

is nothing less than the chemical elements commonly so called, the bodies as yet undecomposed into anything simpler than themselves. There they extend before us, as stretched the wide Atlantic before the gaze of Columbus, mocking, taunting, and murmuring strange riddles, which no man yet has been able to solve.

The first riddle, then, which we encounter in chemistry is, 'What are the elements?' Of the attempts hitherto made to define or explain an element none satisfy the demands of the human intellect. The text-books tell us that an element is 'a body which has not been decomposed'; that it is 'a something to which we can add, but from which we can take away nothing,' or 'a body which increases in weight with every chemical change.' Such definitions are doubly unsatisfactory: they are provisional, and may cease to-morrow to be applicable in any given case. They take their stand, not on any attribute of the things to be defined, but on the limitations of human power; they are confessions of intellectual impotence.

Just as to Columbus long philosophic meditation led him to the fixed belief of the existence of a yet untrodden world beyond that waste of Atlantic waters, so to our most keen-eyed chemists, physicists, and philosophers a variety of phenomena suggest the conviction that the elements of ordinary assumption are not the ultimate boundary in this direction of the knowledge which man may hope to attain. Well do I remember, soon after I had obtained evidence of the distinct nature of thallium, that Faraday said to me, 'To discover a new element is a very fine thing, but if you could decompose an element and tell us what it is made of—that would be a discovery indeed worth making.' And this was no new speculation of Faraday's, for in one of his early lectures he remarked, 'At present we begin to feel impatient, and to wish for a new state of chemical elements. For a time the desire was to add to the metals, now we wish to diminish their number. . . . To decompose the metals, then, to reform them, to change them from one to another, and to realise the once absurd notion of transmutation are the problems now given to the chemist for solution.'

Mr. Herbert Spencer, in his hypothesis of the constitution of matter, says:—'All material substances are divisible into so-called elementary substances composed of molecular particles of the same nature as themselves; but these molecular particles are complicated structures consisting of congregations of truly elementary atoms, identical in nature and differing only in position, arrangement, motion, &c., and the molecules or chemical atoms are produced from the true or physical atoms by processes of evolution under conditions which chemistry has not yet been able to reproduce.'

Mr. Norman Lockyer has shown, I think on good evidence, that, in the heavenly bodies of the highest temperature, a large number of our reputed elements are dissociated, or, as it would perhaps be better to say, have never been formed. Mr. Lockyer holds that 'the temperature of the sun and the electric arc is high enough to dissociate some of the so-called chemical elements, and give us a glimpse of the spectra of their bases'; and he likewise says that 'a terrestrial element is an exceedingly complicated thing that is broken up into simpler things at the temperature of the sun, and some of these things exist in some sun-spots, while other constituents exist in others.'

The late Sir Benjamin Brodie, in a lecture on Ideal Chemistry delivered before the Chemical Society in 1867, goes even further than this. He says:—'We may conceive that, in remote time or in remote space, there did exist formerly, or possibly do exist now, certain simpler forms of matter than we find on the surface of our globe— α , χ , ξ , ν , and so on. . . . We may consider that in remote ages the temperature of matter was much higher than it is now, and that these other things existed then in the state of perfect gases—separate existences—uncombined. . . . We may then conceive that the temperature began to fall, and these things to combine with one another and to enter into new forms of existence, appropriate to the circumstances in which they were placed. . . . We may further consider that, as the temperature went on falling, certain forms of matter became more permanent and more stable, to the exclusion of other forms. . . . We may conceive of this process of the lowering of the temperature going on, so that these substances,

when once formed, could never be decomposed—in fact, that the resolution of these bodies into their component elements could never occur again. You would then have something of our present system of things. . . .

'Now this is not purely an imagination, for when we look upon the surface of our globe we have actual evidence of similar changes in Nature. . . . When we look at some of the facts which have been revealed to us by the extraordinary analyses which have been made of the matter of distant worlds and nebulae, by means of the spectroscope, it does not seem incredible to me that there may even be evidence, some day, of the independent existence of such things as χ and ν .'

In his Burnett Lectures 'On Light as a Means of Investigation,' Professor Stokes, speaking of a line in the spectrum of the nebulae, says:—'It may possibly indicate some form of matter more elementary than any we know on earth. There seems no *à priori* improbability in such a supposition so great as to lead us at once to reject it. Chemists have long speculated on the so-called elements, or many of them, being merely very stable compounds of elements of a higher order, or even perhaps of a single kind of matter.'

In 1868 Graham wrote of Sir W. Thomson's vortex-ring theory, as enlivening 'matter into an individual existence and constituting it a distinct substance or element.'

From these passages, which might easily be multiplied, it plainly appears that the notion—not necessarily of the decomposability, but at any rate of the complexity of our supposed elements—is, so to speak, in the air of science, waiting to take a further and more definite development. It is important to keep before men's minds the idea of the genesis of the elements; this gives some form to our conceptions, and accustoms the mind to look for some physical production of atoms. It is still more important, too, to keep in view the great probability that there exist in Nature laboratories where atoms are formed and laboratories where atoms cease to be. We are on the track and are not daunted, and fain would we enter the mysterious region which ignorance tickets 'Unknown.' It is for us to strive to unravel the secret composition even of the so-called elements—to undauntedly persevere—and 'still bear up right onward.'

If we adopt the easy-going assumption that the elements, whether self-existent or created, are absolutely and primordially distinct; that they existed as we now find them prior to the origin of stars and their attendant planets, constituting, in fact, the primal 'fire-mist,' we are little, if any, the wiser. We look at their number and at their distinctive properties, and we ask, Are all these points accidental or determinate? In other words, might there as well have been only 7, or 700, or 7,000 absolutely distinct elements as the 70 (in round numbers) which we now commonly recognise? The number of the elements does not, indeed, commend itself to our reason from any *à priori* or extraneous considerations. Might their properties have conceivably differed from those which we actually observe? Are they formed by a 'fortuitous concatenation,' or do they constitute together a definite whole, in which each has its proper part to play, and from which none could be extruded without leaving a recognisable deficiency?

If their peculiarities were accidental it would scarcely be possible for the elements to display those mutual relations which we find brought into such prominent light and order in the periodic classification of Newlands, Mendeleeff, and Meyer. Has not the relation between the atomic weights of the three halogens, chlorine, bromine, and iodine, and their serially varying properties, physical and chemical, been worn nearly threadbare? And the same with the calcium and the sulphur groups? Surely the probability of such relations existing among some 70 bodies which had come into fortuitous existence would prove to be vanishingly small!

We ask whether these elements may not have been evolved from some few antecedent forms of matter—or possibly from only one such—just as it is now held that all the innumerable variations of plants and animals have been developed from fewer and earlier forms of organic life? As Dr. Gladstone well puts it, they 'have been built up one from another, according to some general plan.' This building up, or evolution, is above all things not fortuitous: the variation and

development which we recognise in the universe run along certain fixed lines which have been preconceived and foreordained. To the careless and hasty eye design and evolution seem antagonistic; the more careful inquirer sees that evolution, steadily proceeding along an ascending scale of excellence, is the strongest argument in favour of a preconceived plan.

The array of the elements cannot fail to remind us of the general aspect of the organic world. In both cases we see certain groups well filled up, even crowded, with forms having among themselves but little specific difference. On the other hand, in both, other forms stand widely isolated. Both display species that are common and species that are rare; both have groups widely distributed—it might be said cosmopolitan—and other groups of very restricted occurrence. Among animals I may mention as instances the Monotremata of Australia and New Guinea, and among the elements the metals of the so-called rare earths.

Now, as these facts in the distribution of organic forms are generally considered by biological experts to rank among the weightiest evidences in favour of the origin of species by a process of evolution, it seems natural, in this case as in the other, to view existing elements not as primordial but as the gradual outcome of a process of development, possibly even of a 'struggle for existence.' Bodies not in harmony with the present general conditions have disappeared, or perhaps have never existed. Others—the asteroids among the elements—have come into being, and have survived, but only on a limited scale; whilst a third class are abundant because surrounding conditions have been favourable to their formation and preservation.

The analogy here suggested between elements and organisms is, indeed, not the closest, and must not be pushed too far. From the nature of the case there cannot occur in the elements a difference corresponding to the difference between living and fossil organic forms. The 'great stone book' can tell us nothing of extinct elements. Nor would I for a moment suggest that any one of our present elements, however rare, is like a rare animal or plant in process of extinction; that any new element is in the course of formation, or that the properties of existing elements are gradually undergoing modification. All such changes must have been confined to that period so remote as not to be grasped by the imagination, when our Earth, or rather the matter of which it consists, was in a state very different from its present condition. The epoch of elemental development is decidedly over, and I may observe that in the opinion of not a few biologists the epoch of organic development is verging upon its close.

Making, however, every allowance for these distinctions, if evolution be a cosmic law, manifest in heavenly bodies, in organic individuals, and in organic species, we shall in all probability recognise it, though under especial aspects, in those elements of which stars and organisms are in the last resort composed.

Is there, then, in the first place, any direct evidence of the transmutation of any supposed 'element' of our existing list into another, or of its resolution into anything simpler?

To this question I am obliged to reply in the negative.

I doubt whether any chemist here present could suggest a process which would hold out a reasonable prospect of dissociating any of our accepted simple bodies. The highest temperatures and the most powerful electric currents at our disposal have been tried, and tried in vain. At one time there seemed a possibility at least that the interesting researches of Prof. Victor Meyer might show the two higher members of the halogen group, bromine and iodine, as entering upon the path of dissociation. These hopes have not been fulfilled. It may be said, in the general opinion of the most eminent and judicious chemists, that none of the phenomena thus elicited prove that even an approach has been made to the object in view.

Even if we leave our artificial laboratories and seek an escape from the difficulty by observing the processes of the great laboratories of Nature, we feel no sufficiently firm ground.

We find ourselves thus driven to indirect evidence—to that which we may glean from the mutual relations of the elementary bodies. Such evidence of great value is by no means lacking, and to this I now beg to direct attention. First, we

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may consider the conclusion arrived at by Herschel, and pursued by Clerk-Maxwell, that atoms bear the impress of manufactured articles. Let us look a little more closely at this view. A manufactured article may well be supposed to involve a manufacturer. But it does something more: it implies certainly a raw material, and probably, though not certainly, the existence of by-products, residues, *paraleipomena*. What or where is here the raw material? Can we detect any form of matter which bears to the chemical elements a relation like that of a raw material to the finished product—like that, say, of coal-tar to alizarin? Or can we recognise any elementary bodies which seem like waste or refuse? Or are all the elements, according to the common view coequal? To these questions no direct answer is as yet forthcoming.

And this leads us up to a hypothesis which, if capable of full demonstration, would show us that the accepted elements are not coequal, but have been formed by a process of expansion or evolution. I refer to the well-known hypothesis of Prout, which regards the atomic weights of the elements as multiples, by a series of whole numbers, of unity = the atomic weight of hydrogen. Everyone is aware that the recent more accurate determinations of the atomic weights of different elements do not by any means bring them into close harmony with the values which Prout's law would require. Still in no small number of cases the actual atomic weights approach so closely to those which the hypothesis demands that we can scarcely regard the coincidence as accidental. Accordingly, not a few chemists of admitted eminence consider that we have here an expression of the truth, masked by some residual or collateral phenomena which we have not yet succeeded in eliminating.

The original calculations on which the most accurate numbers for the atomic weights are founded have recently been recalculated by Mr. F. W. Clarke. In his concluding remarks, speaking of Prout's law, Mr. Clarke says that 'none of the seeming exceptions are inexplicable. In short, admitting half-multiples as legitimate, it is more probable that the few apparent exceptions are due to undetected constant errors than that the great number of close agreements should be merely accidental. I began this recalculation of the atomic weights with a strong prejudice against Prout's hypothesis, but the facts as they came before me have forced me to give it a very respectful consideration.'

But if the evidence in favour of Prout's hypothesis in its original guise is deemed insufficient, may not Mr. Clarke's suggestion of half-multiples place it upon an entirely new basis? Suppose that the unit of the scale, the body whose atomic weight, if multiplied by a series of whole numbers, gives the atomic weights of the remaining elements, is not hydrogen, but some element of still lower atomic weight? We are here at once reminded of helium—an element purely hypothetical as far as our Earth is concerned, but supposed by many authorities, on the faith of spectroscopic observations, to exist in the sun and in other stellar bodies. Most solar eruptions present merely the characteristic lines of hydrogen C, F, and H, and along with them one particular line which at first was classed in the sodium group, but which is a little more refrangible, and is designated by the symbol D₂. According to Mr. Norman Lockyer and the late Father Secchi, this ray undergoes modifications not comparable to those affecting other rays of the chromosphere. In the corresponding region of the spectrum no dark ray has been observed. That the accompanying lines C, F, and H pertain to hydrogen is evident; and as D₂ has never been obtained in any other spectrum, it is supposed to belong to a body foreign to our Earth, though existing in abundance in the chromosphere of the sun. To this hypothetical body the name helium is assigned.

In an able memoir on this subject, read before the Academy of Brussels, the Abbé E. Spée shows that, if helium exists, it enjoys two very remarkable properties. Its spectrum consists of a single ray, and its vapour possesses no absorbent power. The simple single ray, though I believe unexampled, is by no means an impossible phenomenon, and indicates a remarkable simplicity of molecular constitution. The non-absorbent property of its vapour seems to be a serious objection to a general physical law. Professor Tyndall has demonstrated that the absorptive power

increases with the complexity of molecular structure, and hence he draws the conclusion that the simpler the molecule the feebler the absorption. This conclusion the Abbé Spée regards as perfectly legitimate; but it neither explains nor even necessitates the absence of *all* absorptive power.

Granting that helium exists, all analogy points to its atomic weight being below that of hydrogen. Here, then, we may have the very element, with atomic weight half that of hydrogen, required by Mr. Clarke as the basis of Prout's law.

But a more important piece of evidence for the compound nature of the chemical elements has yet to be considered. Many chemists must have been struck with certain peculiarities in the occurrence of the elements in the Earth's crust; it is a stale remark that we do not find them evenly distributed throughout the globe. Nor are they associated in accordance with their specific gravities; the lighter elements placed on or near the surface, and the heavier ones following serially deeper and deeper. Neither can we trace any distinct relation between local climate and mineral distribution. And by no means can we say that elements are always or chiefly associated in nature in the order of their so-called chemical affinities; those which have a strong tendency to form with each other definite chemical combinations being found together, whilst those which have little or no such tendency exist apart. We certainly find calcium as carbonate and sulphate, sodium as chloride, silver and lead as sulphides; but why do we find certain groups of elements with little affinity for each other yet existing in juxtaposition or commixture? The members of some of these groups are far from plentiful, not generally or widely diffused, and certainly they are not easy to separate.

As instances of such grouping we may mention—

1. Nickel and cobalt, of which it may be said that had their compounds been colourless they would have been long regarded as identical, and possibly even yet would not have been separated.

2. The two groups of platinum metals.

3. The so-called 'rare earths,' occurring in gadolinite, samarskite, &c. and evidently becoming more numerous the more closely they are examined.

Certain questions here suggest themselves:—Is the series of these elements like a staircase or like an inclined plane? Will they, the more closely they are scrutinised, be found to fade away the more gradually the one into the other? Further, will a mixture hitherto held to be simple, like (*e.g.*) didymium, be capable of being split up in one direction only, or in several? I have been led to ask this last question because I have separated from didymium bodies which seem to agree neither with the praseodymium and neodymium of Dr. Auer von Welsbach, nor with the components detected by M. de Boisbaudran and M. Demarçay.

Why, then, are these respective elements so closely associated? What agency has brought them together?

An eminent physicist evades the difficulty by suggesting that their joint occurrence is simply an instance of the working of the familiar principle 'Birds of a feather flock together.' In their chemical and physical attributes these rare earths are so closely similar that they may be regarded as substantially identical in all the circumstances of solution and precipitation to which they may have been exposed during geological ages.

But do we, in point of fact, recognise any such agency at work in Nature? Is there any power which regularly and systematically sorts out the different kinds of matter from promiscuous heaps, conveying like to like and separating unlike from unlike? I must confess that I fail to trace any such distributive agency, nor, indeed, do I feel able to form any distinct conception of its nature.

I must here remark that coral worms in some cases do effect a separation of certain kinds of matter. Thus a *Gorgonia* of the species *Melithæa*, and *Mussa sinuosa*, undoubtedly eliminate from sea-water not merely lime, but even yttria; and other recent corals, *Pocillopora damicornis*, and a *Symphylia* close to the yttria-secreting *Mussa*, separate samaria from sea-water. Sea-weeds and aquatic mollusks contain a larger proportion of iodine and bromine than the waters which they

inhabit, and may thus be said to separate out these elements from the chlorine with which they are mingled.

But if we examine these cases of elimination we see that they are limited in their scope. They extend only to substances existing in solution, of which there is a fresh supply always at hand, and which are capable of entering into the animal or vegetable economy. Again, the elimination of iodine and bromine, effected as just described, is of a very imperfect character, and, when such water-plants and animals die and decay, their constituents will be again distributed in the water.

We cannot well consider that nickel and cobalt have been deposited in admixture by organic agency, nor yet the groups iridium, osmium, and platinum—ruthenium, rhodium, and palladium.

Since the earthy metals to which I have referred—such as yttrium, samarium, holmium, erbium, thulium, ytterbium, &c.—are very rare, the probability of their ever having been brought together in some few uncommon minerals discovered only in a few localities must be regarded as trifling indeed, if we suppose that these metals had at any time been widely diffused in a state of great dilution with other matter. The features which we have just recognised in these earths seem to point to their formation severally from some common material placed in conditions in each case nearly identical. The case is strengthened by a consideration of the other groups of elements, also similar in properties, having little affinity for each other and occurring in admixture; either all or at least some of the elements concerned being moreover decidedly rare. Thus we have nickel and cobalt not plentiful or widely distributed; cobalt, perhaps, never found absolutely free from nickel, and *vice versâ*. We have also the two platinum groups, where very similar features prevail.

A weighty argument in favour of the compound nature of the elements is that drawn from a consideration of the compound radicles, or, as they might be called, pseudo-elements. Their similarity with the accepted elements is perfectly familiar to all chemists. If, for example, we suppose that in some age or in some country men of science were cognisant of the existence and of the behaviour of cyanogen, but had not succeeded in resolving it into its constituents, nothing, surely, would prevent their viewing it as an element, and assigning it a place with the halogens. It may fairly be held that if a body which we know to be compound can be found playing the part of an element, this fact lends a certain plausibility to the supposition that the elements also are not absolutely simple. This line of thought, or at least one closely approximating to it, was worked out by Dr. Carnelley in a paper read before this Association at its last meeting. From a comparison of the physical properties of inorganic with those of organic compounds, Dr. Carnelley concludes that '*the elements, as a whole, are analogous to the hydrocarbon radicles.*' This conclusion, if true, he adds, should lead to the further inference that the so-called elements are not truly elementary, being made up of at least two absolute elements, named provisionally A and B. Hence, he argues, it should be possible to build up a series of compounds of these two primary elements which would correspond to what we now call elements. Such an arrangement, to be admissible, would have to fulfil certain conditions:—The secondary elements thus generated from A and B must exhibit the phenomena of periodicity, and the series would have to form octaves; the entire system is bound to display some feature corresponding to the 'odd and even series' of Mendeleeff's classification; the atomic weights must increase across the system from the first to the seventh group; that is, from the positive to the negative end of each series; the atomicity would have to increase from the first to the middle group, and then either increase or decrease to the seventh group; some feature should appear corresponding to the eighth group; and, lastly, the atomic weights in such a system ought to agree with the atomic weights as experimentally determined.

This last condition Dr. Carnelley rightly regards as the most crucial, and he finds his arrangement gives atomic weights which in a majority of instances coincide approximately with the actual atomic weights. Thus out of a total of sixty-one elements whose atomic weights have been determined with at

least approximate accuracy, and whose places in the periodic system are not disputed, twenty-seven agree almost exactly with the actual numbers, whilst nineteen others are not more than one unit astray.

For a detailed consideration of the conclusions which follow from Dr. Carnelley's views I must refer to his paper as read at our last meeting. Two points bear more especially upon the subject now under consideration—that is, if this speculation on the genesis of the elements is well founded. First, the existence of elements of identical atomic weights, isomeric with each other, would be possible; as such Dr. Carnelley mentions respectively nickel and cobalt (now found to have slightly different atomic weights), rhodium and ruthenium, osmium and iridium, and the metals of some of the rare earths. Secondly, in Dr. Carnelley's scheme all the chemical elements save hydrogen are supposed to be composed of two simpler elements, $A = 12$ and $B = -2$. Of these he regards A as a tetrad identical with carbon, and B as a monad of negative weight—perhaps the ethereal fluid of space.

Dr. Carnelley's three primary elements therefore are carbon, hydrogen, and the ether.

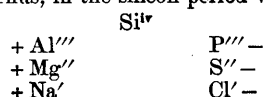
Starting from the supposition that pristine matter was once in an intensely heated condition, and that it has reached its present state by a process of free cooling, Dr. E. J. Mills suggests that the elements as we now have them are the result of successive polymerisations. Dr. Mills reminds us that chemical substances in the process of cooling naturally increase in density, and, if such increase be measured as a function of time or of temperature, we sometimes observe that there are critical points corresponding to the formation of new and well-defined substances. In this manner, ordinary phosphorus is converted into the red variety, I is transformed into I_2 , S_2 becomes S_8 , and NO_2 N_2O_4 . Among organic bodies styrol, in like manner, according to Dr. Mills, is converted into metastyrol, aldehyd into paraldehyd, the cyanates into cyanurates, and turpentine into metaterebenthene. At the critical points above referred to heat is liberated in especial abundance, and the bodies thus formed are known as polymers. If we could gradually cool down substances through a vast range of temperature, we should then probably discover a much greater number of such critical points, or points of multiple proportion, than we have been able to discover experimentally.

The heat given out in the act of polymerisation naturally reverses to some extent the polymerisation itself, and so causes a partial return to the previous condition of things. This forward and backward movement, several times repeated, constitutes 'periodicity.' Dr. Mills regards variable stars as instances, now in evidence, of the genesis of elementary bodies.

From a study of the classification of the elements, Dr. Mills is of opinion that the only known polymers of the primitive matter are arsenic, antimony, and perhaps erbium and osmium; whilst zirconium, ruthenium, samarium, and platinum approximate to the positions of other polymers. Hence, from this genetic view, these elements may be described as products of successive polymerisations.

I must now call attention to a method of illustrating the periodic law, proposed by my friend Professor Emerson Reynolds, of the University of Dublin, which will here assist us. Professor Reynolds points out that in each period the general properties of the elements vary from one to another with approximate regularity until we reach the seventh member, which is in more or less striking contrast with the first element of the same period, as well as with the first of the next. Thus chlorine, the seventh member of Mendeleeff's third period, contrasts sharply both with sodium, the first member of the same series, and with potassium, the first member of the next series; whilst, on the other hand, sodium and potassium are closely analogous. The six elements whose atomic weights intervene between sodium and potassium vary in properties, step by step, until chlorine, the contrast to sodium, is reached. But from chlorine to potassium, the analogue of sodium, there is a change in properties *per saltum*. Further, such alternations of gradual and abrupt transitions are observed as the atomic weights increase. If we thus recognise a contrast in properties—more or less decided—

between the first and the last members of each series, we can scarcely help admitting the existence of a point of mean variation within each system. In general, the *fourth* element of each series possesses the properties we might expect a transition-element to exhibit. If we examine a particular period—for instance, that one whose meso-element is silicon, we note:—*First*, that the three elements of lower atomic weight than silicon, viz. sodium, magnesium, and aluminium, are distinctly *electro-positive* in character, while those of higher atomic weight, viz., phosphorus, sulphur, and chlorine, are as distinctly *electro-negative*. Throughout the best known periods this remarkable subdivision is observable, although, as might be anticipated, the differences become less strongly marked as the atomic weights increase. *Secondly*, that the members above and below the meso-element fall into pairs of elements, which, while exhibiting certain analogies, are generally in more or less direct chemical contrast. Thus, in the silicon period we have—



This division also happens, in many cases, to coincide with some characteristic valence of the contrasted elements. It is noteworthy, however, that the members on the electro-negative side exhibit the most marked tendency to variation in atom-fixing power, so that valence alone is an untrustworthy guide to the probable position of an element in a period.

Thus for the purpose of graphic translation Professor Reynolds considers that the fourth member of a period—silicon, for example—may be placed at the apex of a symmetrical curve, which shall represent, for that particular period, the direction in which the properties of the series of elements vary with rising atomic weights.

In the drawing before you (fig. 1) I have modified Professor Reynolds's diagram in one or two points. I have turned it the reverse way, as it is more convenient to start from the top and proceed downwards. I have represented the pendulous swing as gradually declining in amplitude according to a mathematical law, and I have introduced another half-swing of the pendulum between cerium and lead, which not only renders the oscillations more symmetrical, but brings gold, mercury, thallium, lead, and bismuth on the side where they are in complete harmony with members of foregoing groups, instead of being out of harmony with them. This modification has another advantage, inasmuch as it leaves many gaps to be hereafter filled in with new elements just when the development of research is beginning to demand room for such expansion.

I do not, however, wish to infer that the gaps in Mendeleeff's table, and in this graphic representation of it, necessarily mean that there are elements actually existing to fill up the gaps; these gaps may only mean that at the birth of the elements there was an easy potentiality of the formation of an element which would fit into the place.

Following the curve from hydrogen downwards we find that the elements forming Mendeleeff's eighth group are to be found near three of the ten nodal points. These bodies are 'interperiodic,' both because their atomic weights exclude them from the small periods into which the other elements fall, and because their chemical relations with certain members of the adjacent periods show that they are probably interperiodic in the sense of being transitional.

This eighth group is divided into the three triplets—iron, nickel, and cobalt; rhodium, ruthenium, and palladium; iridium, osmium, and platinum. The members of each triplet have often been regarded as modifications of one single form of matter.

Notice how accurately the series of like bodies fits into this scheme. Beginning at the top, run the eye down analogous positions in each oscillation, taking either the electro-positive or electro-negative swings:—

N	Be	Li	Na	Mg	Al	Si	P	S	Cl	C
V	Ca	K	Cu	Zn	Ga	Ge	As	Se	Br	Ti
Nb	Sr	Rb	Ag	Cd	In	Sn	Sb	Te	I	Zr
—	Ba	Cs	—	—	—	—	—	—	—	—
Ta			Au	Hg	Tl	Pb	Bi			

Notice, also, how orderly the metals discovered by spectrum analysis fit in their places—gallium, indium, and thallium.

The symmetry of nearly all this series proclaims at once that we are working in

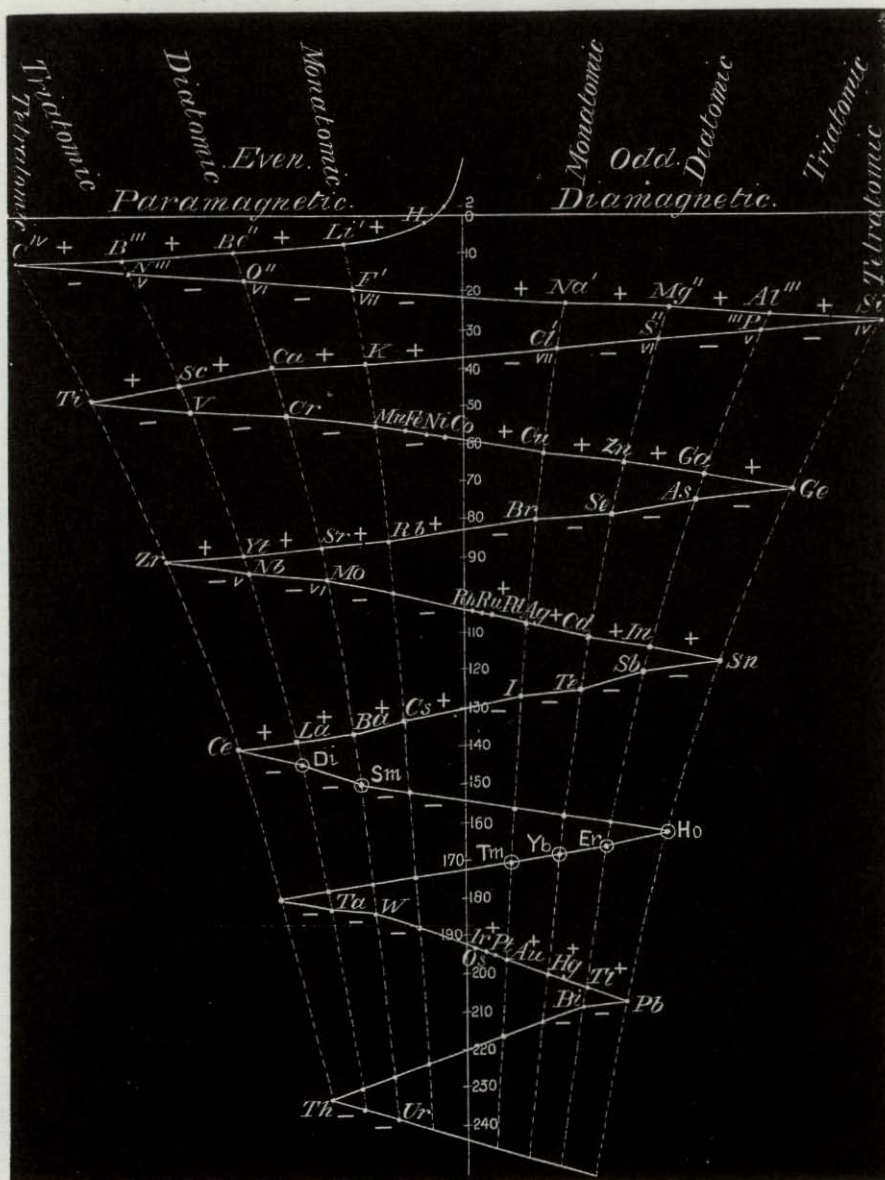


FIG. 1.

the right direction. We can also learn much from the anomalies here visible. Look at the places marked with a circle; didymium, samarium, holmium, erbium,

ytterbium, and thulium. Didymium cannot follow in order after the triad nitrogen, vanadium, columbium; nor erbium follow phosphorus, arsenic, antimony; nor thulium follow chlorine, bromine, iodine; nor ytterbium follow potassium, rubidium, caesium. The inference to be drawn is that these bodies are out of place, owing to their atomic weights not having been correctly determined—an inference which is strengthened by the knowledge that the elementary character of some of these bodies is more than doubtful, whilst the chemical attributes of most of them are unknown.

The more I study the arrangement of this zigzag curve the more I am convinced that he who grasps the key will be permitted to unlock some of the deepest mysteries of creation. Let us imagine if it is possible to get a glimpse of a few of the secrets here hidden. Let us picture the very beginnings of time, before geological ages, before the earth was thrown off from the central nucleus of molten fluid, before even the sun himself had consolidated from the original *protyle*.¹ Let us still imagine that at this primal stage all was in an ultragaseous state, at a temperature inconceivably hotter² than anything now existing in the visible universe; so high, indeed, that the chemical atoms could not yet have been formed, being still far above their dissociation-point. In so far as *protyle* is capable of radiating or reflecting light, this vast sea of incandescent mist, to an astronomer in a distant star, might have appeared as a nebula, showing in the spectroscope a few isolated lines, forecasts of hydrogen, carbon, and nitrogen spectra.

But in course of time some process akin to cooling, probably internal, reduces the temperature of the cosmic *protyle* to a point at which the first step in granulation takes place; matter, as we know it, comes into existence, and atoms are formed. As soon as an atom is formed out of *protyle* it is a store of energy, potential (from its tendency to coalesce with other atoms by gravitation or chemically) and kinetic (from its internal motions). To obtain this energy the neighbouring *protyle* must be refrigerated by it,³ and thereby the subsequent formation of other atoms will be accelerated. But with atomic matter the various forms of energy which require matter to render them evident begin to act; and, amongst others, that form of energy which has for one of its factors what we now call *atomic weight*. Let us assume that the elementary *protyle* contains within itself the potentiality of every possible combining proportion or atomic weight. Let it be granted that the whole of our known elements were not at this epoch simultaneously created. The easiest formed element, the one most nearly allied to the *protyle* in simplicity, is first born. Hydrogen—or shall we say helium?—of all the known elements the one of simplest structure and lowest atomic weight, is the first to come into being. For some time hydrogen would be the only form of matter (as we now know it) in existence, and between hydrogen and the next formed element there would be a considerable gap in time, during the latter part of which the element next in order of simplicity would be slowly approaching its birth-point: pending this period we may suppose that the evolutionary process which soon was to determine the birth of a new element would also determine its atomic weight, its affinities, and its chemical position.

¹ We require a word, analogous to protoplasm, to express the idea of the original primal matter existing before the evolution of the chemical elements. The word I have ventured to use for this purpose is compounded of *πρό* (*earlier than*) and *ἔλγ* (*the stuff of which things are made*). The word is scarcely a new coinage, for 600 years ago Roger Bacon wrote in his *De Arte Chymica*, 'The elements are made out of *ἔλγ*, and every element is converted into the nature of another element.'

² I am constrained to use words expressive of high temperature; but I confess I am unable clearly to associate with *protyle* the idea of hot or cold. *Temperature radiation*, and *free cooling* seem to require the periodic motions that take place in the chemical atoms; and the introduction of centres of periodic motion into *protyle* would constitute its being so far changed into chemical atoms.

³ I am indebted to my friend G. Johnstone Stoney, F.R.S., for the idea here put forward, as well as for other valuable suggestions and criticisms on some of the theoretical questions here treated of.

In the original genesis the longer the time occupied in that portion of the cooling down during which the hardening of the *protyle* into atoms took place, the more sharply defined would be the resulting elements; and, on the other hand, with more irregularity in the original cooling, we should have a nearer approach to the state of the elemental family such as we know it at present.

In this way it is conceivable that the succession of events which gave us such groups as platinum, osmium, and iridium—palladium, ruthenium, and rhodium—iron, nickel, and cobalt, if the operation of genesis had been greatly more prolonged, would have resulted in the birth of only one element of these groups. It is also probable that by a much more rapid rate of cooling, elements would originate even more closely related than are nickel and cobalt, and thus we should have formed the nearly allied elements of the cerium, yttrium, and similar groups; in fact the minerals of the class of samarskite and gadolinite may be regarded as the cosmical lumber-room where the elements in a state of arrested development—the unconnected missing links of inorganic Darwinism—are finally aggregated.

I have said that the original *protyle* contained within itself the potentiality of all possible atomic weights. It may well be questioned whether there is an absolute uniformity in the mass of every ultimate atom of the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic weights of the atoms vary within certain narrow limits.

Each well-defined element represents a platform of stability connected by ladders of unstable bodies. In the first accreting together of the primitive stuff the smallest atoms would form, then these would join together to form larger groups, the gulf across from one stage to another would be gradually bridged over, and the stable element appropriate to that stage would absorb, as it were, the unstable rungs of the ladder which led up to it. I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. We are here reminded of Newton's 'old worn particles.'

Is it not possible, or even feasible, that these heavier and lighter atoms may have been in some cases subsequently sorted out by a process resembling chemical fractionation? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but also it may have been partly effected in geological ages by successive solutions and reprecipitations of the various earths.

This may seem an audacious speculation, but I do not think it is beyond the power of chemistry to test its feasibility. An investigation on which I have been occupied for several years has yielded results which to me appear apposite to the question, and I therefore beg permission here to allude briefly to some of the results, reserving details to a subsequent communication to the Section.

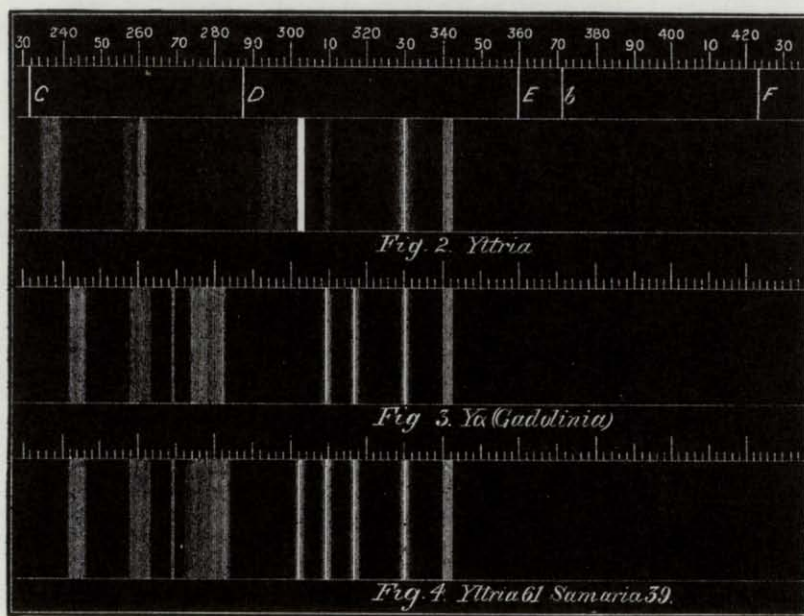
My work has been with the earths present in samarskite and gadolinite, separating them by systematic fractionation. Chemical fractionation, on which I hope to say more on another occasion, is very similar to the formation of a spectrum with a wide slit and a succession of shallow prisms. The centre portion remains unchanged for a long time, and the only approach to purity at first is at the two ends, while a considerable series of operations is needed to produce an appreciable change in the centre. The groups of didymium and yttrium earths are those which have chiefly occupied my attention. On comparing these rare earths we are at once struck with the close mutual similarity, verging almost into identity, of the members of the same group.

The phosphorescent spectra of these earths when their anhydrous sulphates are submitted to the induction discharge *in vacuo* are extremely complicated, and change in their details in a puzzling manner. For many years I have been persistently groping on in almost hopeless endeavour to get a clue to the meaning I felt convinced was locked up in these systems of bands and lines. It was impossible to divest myself of the conviction that I was looking at a series of autograph inscriptions from the molecular world, evidently of intense interest, but written in a strange

and baffling tongue. All attempts to decipher the mysterious signs were, however, for a long time fruitless. I required a Rosetta stone.

Down to a date comparatively recent nothing was more firmly fixed in my mind than the notion that yttria was the oxide of a simple body, and that its phosphorescent spectrum gave a definite system of coloured bands, such as you see in the drawing before you (fig. 2). Broadly speaking, there is a deep red band, a red band, a very luminous citron-coloured band, a pair of greenish-blue bands, and a blue band. It is true these bands varied slightly in relative intensities and in sharpness with almost every sample of yttria I examined; but the general character of the spectrum remained unchanged, and I had got into the way of looking upon this spectrum as characteristic of yttria: all the bands being visible when the earth was present in quantity, whilst only the strongest band of all—the citron band—was visible when traces, such as millionths, were present. But that the whole system of bands spelled yttria, and nothing but yttria, I was firmly convinced.

During the later fractionations of the yttria earths, and the continued observations of their spectra, certain suspicions which had troubled me for some time



assumed consistent form. The bands which hitherto I had thought belonged to yttria began to vary in intensity among themselves, and continued fractionation increased the differences first observed. Whilst I was in this state of doubt and uncertainty, and only beginning to see my way towards arranging into a consistent whole the facts daily coming to light, help came from an unexpected quarter. M. de Marignac, with whom I had been for some time in correspondence, kindly sent me a small specimen of the earth which he had discovered and provisionally named *Ya* (now *Gadolinia*). In the radiant-matter tube this earth gave a bright spectrum, like the one in the diagram before you (fig. 3). The spectrum above it (fig. 2) is that ascribed to yttria. Look at the two. Omitting minor details, *Ya* is yttria with the chief characteristic band—the citron band—left out, and with the double green band of samaria added to it. Now look at fig. 4, which represents the spectrum of a mixture of sixty-one parts of yttria and thirty-nine parts of samaria. It is identical almost to its minutest detail with the spectrum of *Ya*,

with this not unimportant difference—the citron band is as prominent as any other line. Ya consists, therefore, of samaria with the greenish blue of yttria and some of the other yttria bands added to it.

I may aptly call the Ya spectrum my Rosetta stone. It threw a flood of light on all the obscurities and contradictions I had found so plentiful, and showed me that a much wider law than the one I had been working upon was the true law governing the occurrence of these obscure phenomena. For what does the spectrum of Ya show? It proves that what I had hitherto thought was one of the chief bands in the yttria spectrum—the citron band—could be entirely removed, whilst another characteristic group—the double green of yttria—could also be separated from the citron.

It would exceed legitimate limits were I to enter into details respecting the chemical and physical reasons which led me to these definite conclusions. To settle one single point more than 2,000 fractionations have been performed.

The meaning of the strongly marked symbolic lines had first to be ascertained. For a long time I had to be content with roughly translating one group of coloured symbols as 'yttrium' and another group as 'samarium,' disregarding the fainter lines, shadows, and wings frequently common to both. Constant practice in the decipherment has now given me fuller insight into what I may call the grammar of these hieroglyphic inscriptions. Every line and shadow of a line, each faint wing attached to a strong band, and every variation in intensity of the shadows and wings among themselves, now has a definite meaning which can be translated into the common symbolism of chemistry.

In a mineral containing the rarer earths those most widely separated in chemical properties are most easily obtained in a state of comparative purity by simple chemical means. For instance, in separating didymium from lanthanum, or samarium from yttrium, a few simple chemical reactions and a little waste will give these bodies in a state of purity: but when it comes to splitting up yttrium into its components ordinary chemical separation is useless, and fractionation must be pushed to the utmost limit, many thousand operations and enormous waste of material being necessary to effect even a partial separation.

Returning, therefore, after this explanatory digression, to the idea of heavy and light atoms, we see how well this hypothesis accords with the new facts here brought to light. From every chemical point of view the stable molecular group, yttrium, behaves as an element. Excessive and systematic fractionation has acted the part of a chemical 'sorting Demon,' distributing the atoms of yttrium into several groups, with certainly different phosphorescent spectra, and presumably different atomic weights, though all these groups behave alike from the usual chemical point of view. Here, then, is one of the elements the spectrum of which does not emanate equally from all its atoms, but some atoms furnish some, other atoms others, of the lines and bands of the compound spectrum of the element. And as this is the case with one element, it is probably so in a greater or less degree with all. Hence the atoms of this element differ probably in weight, certainly in the internal motions they undergo.

Another important inference which may be drawn from the facts is that the atoms of which yttrium consists, though differing, do not differ continuously, but *per saltum*. We have evidence of this in the fact that the spectroscopic bands characteristic of each group are distinct from those of the other groups, and do not pass gradually into them. We must accordingly expect, in the present state of science, that this is probably the case with the other elements. And the atoms of a chemical element being known to differ in one respect may differ in other respects, and presumably do somewhat differ in mass.

Restricted by limited time and means, even a partial separation of these atomic groupings is possible to me only with enormous difficulty. Have we any evidence that Nature has effected such a separation? The following facts I think supply this evidence.

The earth yttria occurs in several minerals, all extremely rare. These minerals are of very diverse chemical composition, and occur in localities widely separated geographically. Does the pure yttria (*pure* in respect to every other known

element) from these different sources behave differently to the radiant-matter test? To the chemist hitherto the earth yttria has been the same thing and has possessed the same properties, whatever its source; but armed with this new power of seeing into the atomic groupings which go to make up yttrium, we find evidence of differentiation between one yttrium and another.

Thus when the samarskite yttrium was formed all the constituent atoms—deep red, red, orange, citron, greenish-blue, and blue¹—condensed together in fair proportion, the deep red being faintest. In gadolinite yttrium the citron and greenish-blue constituents are plentiful, the red is very deficient, the orange is absent, and the others occur in moderate quantities. In the yttrium from xenotime the citron is most plentiful, the greenish-blue occurs in smaller proportion, the red is all but absent, and the orange is quite absent. Yttrium from monazite contains the greenish-blue and citron, with a fair proportion of the other constituents; the greenish-blue is plentiful, and the red is good. Yttrium from fluocerite is very similar to that from monazite, but the blue is weaker. Yttrium from hielmite is very rich in citron, has a fair quantity of blue and greenish-blue, less of red, no orange, and only a very faint trace of deep red. Yttria from euxenite is almost identical with that from hielmite. Yttria from cerite contains most red and citron, a fair amount of orange, less greenish-blue and blue, and only a trace of deep red.

This is unlikely to be an isolated case. The principle is very probably of general application to all the elements. In some, possibly in all elements, the whole spectrum does not emanate from all its atoms, but different spectral rays may come from different atoms, and in the spectrum as we see it all these partial spectra are present together. This being interpreted means that there are definite differences in the internal motions which go on in the several groups of which the atoms of a chemical element consist. For example, we must now be prepared for some such events as that the seven series of bands in the absorption-spectrum of iodine may prove not all to emanate from every molecule, but that some of these molecules emit some of these series, others others, and in the jumble of all these kinds of molecules, to which is given the name 'iodine vapour,' the whole seven series are contributors.

To me it appears the theory I have here ventured to formulate, taken in conjunction with the diagram in fig. 1, may aid the scientific imagination to proceed a step or two further in the order of elemental evolution. In the undulating curve may be seen the action of two forces, one acting in the direction of the vertical line, and the other pulsating backwards and forwards like a pendulum. Assume the vertical line to represent temperature slowly sinking through an unknown number of degrees, from the dissociation-point of the first-formed element down to the dissociation-point of those last shown on the scale. But what form of energy is represented by the oscillating line? Swinging to and fro like a mighty pendulum to points equidistant from a neutral centre; the divergence from neutrality conferring atomicity of one, two, three, and four degrees as the distance from the centre is one, two, three, or four divisions; and the approach to, or retreat from, the neutral line deciding the electro-negative or electro-positive character of the element—all on the retreating half of the swing being positive and all on the approaching half negative—this oscillating force must be intimately connected with the imponderable matter, essence, or source of energy we call electricity.

Let us examine this a little more closely. Let us start at the moment when the first element came into existence. Before this time matter, as we know it, was not. It is equally impossible to conceive of matter without energy, as of energy without matter; from one point of view the two are convertible terms. Before the birth of atoms all those forms of energy which become evident when matter acts upon matter could not have existed—they were locked up in the *protyle* as latent potentialities only. Coincident with the creation of atoms all those attributes and properties which form the means of discriminating one chemical element from another start into existence fully endowed with energy.

¹ For brevity I call them by their dominant spectrum band.

The pendulum begins its swing from the electro-positive side; lithium, next to hydrogen in simplicity of atomic weight, is now formed; then glucinum, boron, and carbon. Definite quantities of electricity are bestowed on each element at the moment of birth, on these quantities its atomicity depends,¹ and the types of monatomic, diatomic, triatomic, and tetratomic elements are fixed. The electro-negative part of the swing now commences; nitrogen appears, and notice how curiously position governs the mean dominant atomicity. Nitrogen occupies the position below boron, a triatomic element, therefore nitrogen is triatomic. But nitrogen also follows carbon, a tetratomic body, and occupies the fifth position counting from the place of origin. How beautifully these opposing tendencies are harmonised by the endowment of nitrogen with at least a double atomicity, and making its atom capable of acting as tri- and pentatomic. With oxygen (di- and hexatomic) and fluorine (mon- and heptatomic) the same law holds, and one-half oscillation of the pendulum is completed. Again passing the neutral line the electro-positive elements sodium (monatomic), magnesium (diatomic), aluminium (triatomic), and silicon (tetratomic) are successively formed, and the first complete oscillation of the pendulum is finished by the birth of the electro-negative elements, phosphorus, sulphur, and chlorine; these three—like the corresponding elements formed on the opposite homeward swing—having each at least a double atomicity depending on position.

Let us pause at the end of the first complete vibration and examine the result. We have already formed the elements of water, ammonia, carbonic acid, the atmosphere, plant and animal life, phosphorus for the brain, salt for the sea, clay for the solid earth, two alkalies, an alkaline earth, an earth, together with their carbonates, borates, nitrates, fluorides, chlorides, sulphates, phosphates, and silicates, sufficient for a world and inhabitants not so very different from what we enjoy at the present day. True, the human inhabitants would have to live in a state of more than Arcadian simplicity, and the absence of calcic phosphate would be awkward as far as bone is concerned. But what a happy world it would be! No silver or gold coinage, no iron for machinery, no platinum for chemists, no copper wire for telegraphy, no zinc for batteries, no mercury for pumps, and, alas! no rare earths to be separated.

The pendulum does not, however, stop at the end of the first complete vibration; it crosses the neutral point, and now the forces at work are in the same position as they were at the beginning. Had everything been as it was at first, the next element again would have been lithium, and the original cycle would have recurred, repeating for ever the same elements. But the conditions are not quite the same; the form of energy represented by the vertical line has declined a little—the temperature has sunk—and not lithium, but the one next allied to it in the series comes into existence—potassium, which may be regarded as the lineal descendant of lithium, with the same hereditary tendencies, but with less molecular mobility and higher atomic weight.

Pass we rapidly along the to and fro curve, and in nearly every case the same law is seen to hold good. The last element of the first complete vibration is chlorine. In the corresponding place in the second vibration we do not have an exact repetition of chlorine, but the very similar body bromine; and when for a third time the position recurs we see iodine. I need not multiply examples.

In this far-reaching evolutionary scheme it could not come to pass that the

¹ 'Nature presents us with a single definite quantity of electricity. . . . For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases.'—G. Johnstone Stoney, 'On the Physical Units of Nature.' *British Association Meeting*, 1874, Section A. *Phil. Mag.*, May 1881.

'The same definite quantity of either positive or negative electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion.'—Helmholtz, Faraday Lecture, 1881.

'Every monad atom has associated with it a certain definite quantity of electricity; every dyad has twice this quantity associated with it; every triad three times as much, and so on.'—O. Lodge, 'On Electrolysis,' *British Association Report*, 1885.

potential elements would all be equal to one another. Some would be unable to resist the slightest disturbance of the unstable equilibrium in which they took their rise; others would endure longer, but would ultimately break down as temperature and pressure varied. Many degrees of stability would be here represented; not all the chemical elements are equally stable, and if we look with scrutinising eyes we shall still see our old friend the missing link, coarse enough to be detected by ordinary chemical processes, associated in the groups containing such elements as iron, nickel, and cobalt; palladium, ruthenium, and rhodium; iridium, osmium, and platinum. Whilst in their more subtle form these missing links present themselves as the representatives of the differences which I have detected and described between the atoms of the same chemical element.

Dr. Carnelley has pointed out that 'those elements belonging to the even series of Mendeleeff's classification are always paramagnetic, whereas the elements belonging to the odd series are always diamagnetic.' On this curve the even series to the left, as far as can be ascertained, are paramagnetic, and, with a few exceptions, all to the right are diamagnetic. The very powerful magnetic metals, iron, nickel, cobalt, and manganese, occur close together on the proper side. The interperiodic groups of which palladium and platinum are examples are said to be feebly magnetic, and if so they form the exceptions. Oxygen, which, weight for weight, is more magnetic than iron, comes near the beginning of the curve, while the powerfully diamagnetic metals, bismuth and thallium, are at the opposite end of the curve.

On the odd, or diamagnetic half of the swing, the energy appears to have considerable regularity, whilst it is very irregular on the opposite side of the curve. Thus, between the extreme odd elements, silicon (28), germanium (73), tin (118), the missing element (163), and lead (208), there is a difference of exactly 45 units, conferring remarkable symmetry on one half of the curve. The differences on the even side are 36, 42, 51, 39, and 53 (giving the missing element between cerium and thorium an atomic weight of 180); these at first sight appear conformable to no law, but they become of great interest when it is seen that the mean difference of these figures is almost exactly the same as that on the other side of the curve—viz. 44.2.

This uniformity of difference—actual on the one side and average on the other—brings out the important inference that, whilst on the odd side there has been little or no variation in the vertical force, minor irregularities have been the rule on the even side. That is to say, the fall of temperature has been very uniform on the odd side—where every element formed during this half of the vibration is the representative of a strongly marked group—sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine; whilst on the even side of the swing the temperature has sunk with considerable fluctuations, which have prevented the formation here of any well-marked groups of elements, with the exception of those of which lithium and glucinum are the types.

If we can thus trace irregularities in the fall of temperature can we also detect any variation in the force represented by the pendulous movement? I have assumed that this represents chemical energy. In the early formed elements we have those in which chemical energy is at its maximum intensity, while, as we descend, affinities for oxygen are getting less and the chemism is becoming more and more sluggish. Part may be due to the lower temperature of generation not permitting such molecular mobility in the elements, but there can be little doubt that the chemism-forming energy, like the fires of the cosmical furnace, is itself dying out. I have endeavoured to represent this gradual fading out by a diminution of amplitude, the curve being traced from a photographic record of the diminution of the arc of vibration of a body swinging in a resisting medium.

When we look on a curve of this kind there is a tendency to ask, what is there above and below the portion which is seen? At the lower end of our curve what is there to be noted? We see a great hiatus between barium (137) and iridium (192.5), which it seems likely will be filled up by the so-called rare elements. Judging from my own researches, it is probable that many of these earthy elements will be found included in one or more interperiodic groups, whilst the higher mem-

bers of the calcium, the potassium, the chlorine, and the sulphur groups, together with the elements between silver and gold, cadmium and mercury, indium and thallium, and antimony and bismuth, are still waiting to be discovered. We now come to an oasis in the desert of blanks. Platinum, gold, mercury, thallium, lead, and bismuth, all familiar friends, form a close little group by themselves, and then after another desert space the list is closed with thorium (233) and uranium (240).

This oasis and the blanks which precede and follow it may be referred with much probability to the particular way in which our Earth developed into a member of our solar system. If this be so it may be that on our Earth only these blanks occur, and not generally throughout the universe.

What comes after uranium? I should consider that there is little prospect of the existence of an element much lower than this. Look at the vertical line of temperature slowly sinking from the upper to the lower part of the curve; the figures representing the scale of atomic weights may be also supposed to represent, inversely, the scale of a gigantic pyrometer dipping into the cauldron where suns and worlds are in process of formation. Our thermometer shows us that the heat has been sinking gradually, and, *pari passu*, the elements formed have increased in density and atomic weight. This cannot go on for an indefinite extent. Below the uranium point the temperature may be so reduced that some of the earlier formed elements which have the strongest affinities are able to enter into combination among themselves, and the result of the next fall in temperature will then be—instead of elements lower in the scale than uranium—the combination of oxygen with hydrogen, and the formation of those known compounds the dissociation of which is not beyond the powers of our terrestrial sources of heat.

Let us now turn to the upper portion of the scheme. With hydrogen of atomic weight = 1, there is little room for other elements, save perhaps for hypothetical helium. But what if we get 'through the looking-glass,' and cross the zero-line in search of new principles—what shall we find the other side of zero? Dr. Carnelley asks for an element of negative atomic weight; here is ample room and verge enough for a shadow series of such unsubstantialities. Helmholtz says that electricity is probably as atomic as matter;¹ is electricity one of the negative elements? and the luminiferous ether another? Matter, as we now know it, does not here exist; the forms of energy which are apparent in the motions of matter are as yet only latent possibilities. A substance of negative weight is not inconceivable.² But can we form a clear conception of a body which combines with other bodies in proportions expressible by negative quantities?

A genesis of the elements such as is here sketched out would not be confined to our little solar system, but would probably follow the same general sequence of events in every centre of energy now visible as a star.

Before the birth of atoms to gravitate towards one another, no pressure could be exercised; but at the outskirts of the fire-mist sphere, within which all is protyle—at the shell on which the tremendous forces involved in the birth of a chemical element exert full sway—the fierce heat would be accompanied by gravitation sufficient to keep the newly-born elements from flying off into space. As temperature increases expansion and molecular motion increase, molecules tend to fly asunder, and their chemical affinities become deadened; but the enormous pressure of the gravitation of the mass of atomic matter outside what I may for brevity call the birth-shell would counteract this action of heat.

Beyond this birth-shell would be a space in which no chemical action could take place, owing to the temperature there being above what is called the dissociation-point for compounds. In this space the lion and the lamb would lie down

¹ 'If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity.'—Helmholtz, Faraday Lecture, 1881.

² 'I can easily conceive that there are plenty of bodies about us not subject to this intermutual action, and therefore not subject to the law of gravitation.'—Sir George Airy. *Faraday's Life and Letters*, vol. ii. p. 354.

together; phosphorus and oxygen would mix without union; hydrogen and chlorine would show no tendency to closer bonds; and even fluorine, that energetic gas which chemists have only isolated within the last month or two, would float about free and uncombined.

Outside this space of free atomic matter would be another shell, in which the formed chemical elements would have cooled down to the combination-point, and the sequence of events so graphically described by Mr. Mattieu Williams in 'The Fuel of the Sun' would now take place, culminating in the solid earth and the commencement of geological time.

And now I must draw to a close, having exhausted not indeed my subject, but the time I may reasonably occupy. We have glanced at the difficulty of defining an element; we have noticed, too, the revolt of many leading physicists and chemists against the ordinary acceptation of the term element. We have weighed the improbability of their eternal self-existence or their origination by chance. As a remaining alternative we have suggested their origin by a process of evolution like that of the heavenly bodies according to Laplace, and the plants and animals of our globe according to Lamarck, Darwin, and Wallace. In the general array of the elements, as known to us, we have seen a striking approximation to that of the organic world. In lack of direct evidence of the decomposition of any element, we have sought and found indirect evidence. We have taken into consideration the light thrown on this subject by Prout's law, and by the researches of Mr. Lockyer in solar spectroscopy. We have reviewed the very important evidence drawn from the distribution and collocation of the elements in the crust of our earth. We have studied Dr. Carnelley's weighty argument in favour of the compound nature of the so-called elements from their analogy to the compound radicles. We have next glanced at the view of the genesis of the elements; and, lastly, we have reviewed a scheme of their origin suggested by Professor Reynolds's method of illustrating the periodic classification.

Summing up all the above considerations we cannot, indeed, venture to assert positively that our so-called elements have been evolved from one primordial matter; but we may contend that the balance of evidence, I think, fairly weighs in favour of this speculation.

This, then, is the intricate question which I have striven to unfold before you, a question which I especially commend to the young generation of chemists, not only as the most interesting but the most profoundly important in the entire compass of our science.

I say deliberately and advisedly the *most interesting*. The doctrine of evolution, as you well know, has thrown a new light upon and given a new impetus to every department of biology, leading us, may we not hope, to anticipate a corresponding wakening light in the domain of chemistry?

I would ask investigators not necessarily either to accept or to reject the hypothesis of chemical evolution, but to treat it as a provisional hypothesis; to keep it in view in their researches, to inquire how far it lends itself to the interpretation of the phenomena observed, and to test experimentally every line of thought which points in this direction. Of the difficulties of this investigation none can be more fully aware than myself. I sincerely hope that this, my imperfect attempt, may lead some minds to enter upon the study of this fundamental chemical question, and to examine closely and in detail what I, as if amidst the clouds and mists of a far distance, have striven to point out.

The following Papers were read:—

1. *On the Absorption Spectra of Uranium Salts.*
By W. J. RUSSELL, F.R.S., and W. LAPRAIK, F.C.S.

Well-marked absorption bands are produced in the visible spectrum by the different salts of this metal. The salts are divided into two very distinct classes, uranous and uranic salts, and each class gives an entirely different absorption spectrum;

FARADAY LECTURE.

(Delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution on Tuesday, April 19th, 1904.)

Elements and Compounds.

By WILHELM OSTWALD.

I have the honour of speaking to an audience of many men whom I have long venerated as my intellectual, although not my personal, teachers, and whom I admire as leaders in our common work for science. But however admirable the *present*, I am still more impressed by the thought of the *past* associated with this place. When, not long ago, I was engaged in electrochemical investigations and almost daily sought for information and enlightenment in Faraday's Researches, I did not dare to think in my boldest dreams that one day I should find myself standing on the very spot in which he was wont to give the first accounts of the innumerable results of his indefatigable labours, his indomitable zeal, and his inexorable love of truth.

All that the pupil can do in such a case is to imbue himself as completely as he can with the ideas of the master and to try to perform his modest work in the master's spirit. But here arises a new difficulty: what subject ought I to choose? When I look into my own humble efforts, I find everywhere traces of Faraday. So far as relates to electrochemistry, the thing is plain; I think there is no word that I have oftener spoken or written than the word "ion," that word which was uttered for the first time in its modern sense in this very spot. But in other fields in which I have also worked, I feel the influence of his skilful hands and his keen vision. Catalysis, which I have studied during the past ten years, likewise came under his hands; and in the parts of the subject he worked at, the charm of secrecy and inexplicableness has been exchanged for the better qualities of a problem capable of resolution by earnest workers. And in one subject which has engrossed a very great part of my scientific activity, in the question of energy, I find the venerated master again a leader. He was indeed the first scientific man to direct all his investigations in view of the idea of the conservation and the mutual transformation of the various forces, as he called them, or the various kinds of energy, as we call them now.

This is a side of Faraday's mind, to which perhaps not so much attention has been paid as it deserves. Although doubtless the greatest advance—the discovery of the quantitative proportionality

between the energy which disappears and that which originates—was due to Mayer and Joule at a later date, yet the practical perception of this relation was working in Faraday's mind long before. There is indeed a great difference between the intellectual development of a scientific truth to a degree sufficient for the discoverer's *own* work, and to the degree required for its successful transfer to the minds of *other* workers. Faraday contented himself in this case, as well as in others (for example, in his conception of lines of force), with the first step. But that he had reached this step and stood firmly on it, that he used this conception constantly and regularly in his work, is evident from his constant reference to it from the first year of his scientific work onwards. From a closer study of his lectures and papers we learn that in every case he put the question: how can I change a given force into another? This continued to the very end of his work; for the last experiments he made related to the direct conversion of gravity into electricity, and although he did not succeed in his attempt, he was nevertheless convinced of the possibility of the conversion.

Guided by these considerations, I directed my attention to the very earliest problems treated by the master. Even before Faraday held the Chair of Chemistry here in the Royal Institution, as a youth of twenty-five years of age he practised the art of a lecturer in a small club, the City Philosophical Society, and the first course which he delivered there was on chemistry. In the sixteenth lecture, after a description of the metals, he concluded with the following general remarks:

"To decompose the metals, then, to reform them, to change them from one to another, and to realise the once absurd notion of transmutation, are the problems now given to the chemist for solution. Let none start at the difficult task and think the means far beyond him; everything may be gained by energy and perseverance." And after a description of how in the course of history the means necessary for the isolation of the metals from their combinations have grown ever more and more efficacious, he mentioned the recent great discoveries of his master Davy as follows:

"Lastly, glance but at the new, the extraordinary powers which the chemist of our own nation put in action so successfully for the reduction of the alkalies and the earths, and you will no longer doubt that powers still more progressive and advanced may exist and put at some favourable moment the bases of the metals in our hands."

When I try to follow this hint and take for the object of our consideration the question of the nature of the elements and of their compounds, I am aware that I am not the first who has done so in this place. If I am not mistaken, the very first chemist who had the honour of addressing you as a Faraday lecturer, Jean-Bap-

tiste Dumas, lectured 35 years ago on the same subject. Nevertheless, I do not shrink from the repetition. Every generation of chemists must form its own views regarding this fundamental problem of our science. The progress of science shows itself in the way in which this is done. Faraday was at this time fully influenced by Humphry Davy's brilliant discoveries, and sought for the solution of the problem in Davy's way. For Dumas, the most important achievement of the science of his day was the systematising of organic chemistry, condensed into the concept of *homologous series*. He therefore regarded the elements as comparable with the hydrocarbon radicles, and tried to arrange them in similar series with constant differences in the numerical values of their atomic weights. It is well known that these ideas finally developed into the great generalisation we owe to Newlands, Lothar Meyer, and Mendeléeff. Although the problem of the decomposition of the elements was not solved in this way, these ideas proved to be most efficient factors in the general development of science.

From what store of ideas will a modern chemist derive the new materials for a new answer to the old question? A physicist will have a ready answer: he will construct the elements in a *mechanical* way, or, if he is of the most modern type, he will use *electricity* as timber. The chemist will look on these structures with due respect indeed, but with some reserve. Long experience has convinced chemists (or at least some of them) that every hypothesis taken from another science ultimately proves insufficient. They are adapted to express certain sides of his, the chemist's, facts, but on other not less important sides they fail, and the end is inadequacy. Learning by this experience, he makes a rule to use only chemical material for this work, and according to this rule I propose to proceed.

Hence, like Dumas, I put the question: what are the most important achievements of the chemistry of our day? I do not hesitate to answer: *chemical dynamics* or the theory of the progress of chemical reactions and the theory of chemical equilibrium. What answer can chemical dynamics give to the old question about the nature of the chemical elements?

The answer to this question sounds most remarkable; and to impress you with the importance I ascribe to this investigation, I will mention the result at once: *It is possible, to deduce from the principles of chemical dynamics all the stoichiometrical laws; the law of constant proportions, the law of multiple proportions and the law of combining weights.* You all know that up to the present time it has only been possible to deduce these laws by help of the atomic hypothesis. Chemical dynamics has, therefore, made the atomic hypothesis

unnecessary for this purpose and has put the theory of the stoichiometrical laws on more secure ground than that furnished by a mere hypothesis.

I am quite aware that in making this assertion I am stepping on somewhat volcanic ground. I may be permitted to guess that among this audience there are only very few who would not at once answer, that they are quite satisfied with the atoms as they are, and that they do not in the least want to change them for any other conception. Moreover, I know that this very country is the birthplace of the atomic hypothesis in its modern form, and that only a short time ago the celebration of the centenary of the atomic hypothesis has reminded you of the enormous advance which science has made in this field during the last hundred years. Therefore I have to make a great claim on your unbiassed scientific receptivity. But still I do not hesitate one moment to lay the results of my work before you. For I feel quite sure that I shall find this receptivity unrestricted; and, moreover, I shall reap another advantage. For I also feel assured that you will offer me the severest criticism which I shall be able to find anywhere. If my ideas should prove worthless, they will be put on the shelf here more quickly than anywhere else, before they can do harm. If, on the contrary, they should contain anything sound, they will be freed here in the most efficacious way from their inexact and inconsistent components, so as to take the shape fittest for lasting use in science. And now let us go into the matter.

The first concept we start from is *equilibrium*. In its original meaning, this word expresses the state of a balance when two loads are of the *same weight*. Later, the conception was transferred to forces of all kinds, and designates the state when the forces neutralise one another in such a way that *no motion* occurs. As the result of the so-called chemical forces does not show itself as a motion, the use of the word has to be extended still further to mean that *no variation* occurs in the properties of the system. In its most general sense, *equilibrium denotes a state independent of time*.

For the existence of such a state it is above all necessary that temperature and pressure shall remain constant; in consequence of this, volume and entropy remain constant too. Now it is a most general experimental law, that the possibility of such a state, independent of time, is dependent on the *homogeneity* of the system. In non-homogeneous bodies, as, for instance, in a solution of different concentrations in different places, or in a gaseous mixture of different composition in different places, equilibrium cannot exist, and the system will change spontaneously into a homogeneous state. We can therefore limit our consideration to this state, and we shall consider

only bodies or systems of bodies in equilibrium, and, consequently, homogeneous.

Perhaps the possibility of the existence of water in contact with water-vapour might be considered contradictory to this statement, because we have here two different states and no homogeneity. Here we meet with the new concept created by Willard Gibbs, namely, that of a *phase*.

Systems of this kind are formed of homogeneous bodies indeed, but of more than one. The water in our system is homogeneous in itself, and the vapour too, and equilibrium cannot exist until both are homogeneous. But there is a possibility that a finite number of different homogeneous bodies can exist together without disturbing one another. In such a system we must have the same temperature and the same pressure everywhere, but the specific volume and the specific entropy may change from one body to the other.

We call a *phase* every part of the system where these specific properties exhibit the same value. It is not necessary that a phase should be connected to one body only; it may be distributed over any number of parts. In this way the millions of globules of butter in milk form only *one* phase, and the watery solution of casein and milk-sugar forms a second phase: milk is a two-phase system.

Every system consisting of only one phase has two degrees of freedom. This law involves only the assumption that the sole forms of energy involved in the system are heat and volume-energy; we exclude from consideration any effects due to gravitation, electricity, surface-tension, &c. This law is connected with the famous phase rule of Willard Gibbs, but is not identical with it, for it contains no mention at all of the so-called components of the system. Indeed, the law is valid in the same way for any pure chemical element, for example, oxygen, or for any mixture, for example, a glass of whisky and water. If you allow to the latter only one phase, it is impossible to change it in more than two ways, namely, in pressure and temperature.

The existence of such a body in the shape of only one phase is generally limited. If the pressure be lowered at constant temperature, a liquid or a solid will change at last into a gas. Lowering of temperature will change a gas into a liquid and a liquid into a solid. For every one-phase system it is possible to determine a "sphere of existence." This sphere is not necessarily limited on all sides; for gases we do not expect a limit on the side of low pressures and high temperatures, nor for solids on the side of high pressures and low temperatures. But on certain sides every phase has its limits, and most of these limits are experimentally accessible.

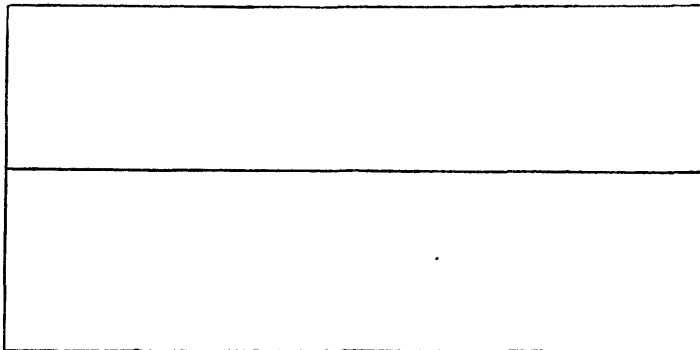
What will happen if we exceed the limit of existence of a phase?

The answer is most simple: *a new phase will be formed*. The spheres of existence of the different phases therefore limit one another, and the boundary-lines represent the interdependent values of temperature and pressure for the possibility of the co-existence of both phases.

By granting the co-existence of two phases we lose therefore one degree of freedom. At the same time a new variation has arisen from the ratio between the masses of the two phases. For we must not suppose that this ratio is without influence on the state; indeed we find here two radically different cases.

The most general case is, that during the transformation of one phase into another the properties of both are continually changing, and the state of every phase is therefore dependent on the ratio of the two masses. By evaporating sea-water at constant temperature the

FIG. 1.



density of the residue grows continually higher, while the pressure, and therefore the density, of the vapour goes on decreasing. If, however, we evaporate distilled water, we do not find any change in the properties of the residue and of the vapour during the whole transmutation.

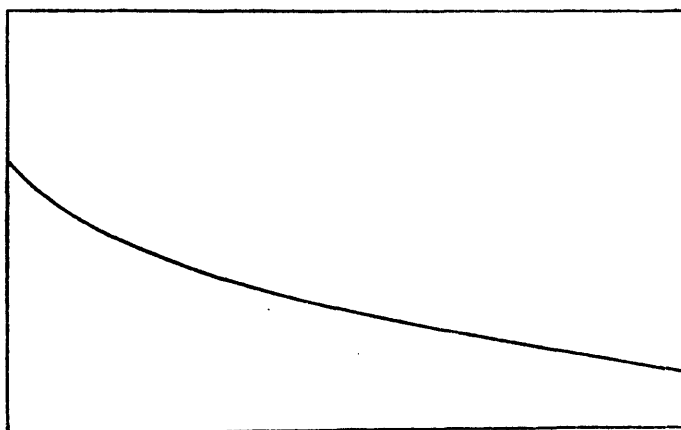
Bodies of the first description we will call *solutions*, and of the second, *hylotropic bodies*. You will be inclined to call the latter substances or chemical individuals, and indeed both concepts are most nearly related. However, the concept of a hylotropic body is somewhat broader than that of a substance. But the possibility of being changed from one phase into another without variation of the properties of the residue and of the new phase is indeed the most characteristic property of a substance or chemical individual, and all our methods of testing the purity of a substance or of preparing a pure one can be reduced to this one property; any one may readily convince him-

M M 2

self of this by investigating any such method in the light of this description.

If we represent these cases by means of rectangular co-ordinates, taking as abscissæ the part of the first phase converted into the second, and as ordinates pressure or temperature, we get Fig. 1 (p. 6) for hylotropic bodies; they are represented by a horizontal straight line. With a solution we get a continuous line too, but not horizontal and generally not straight. If the ordinates are pressures at constant temperature, and the change is from liquid into vapour, the line will slope downwards as Fig. 2 shows. At other temperatures the lines will be of similar shape, only lying higher at higher temperatures and *vice versa*. With other changes we obtain similar lines, sloping upwards or downwards as the case may be. For simplicity's sake we

FIG. 2.



will consider in the future only vaporisation; this case gives the greatest possible variety, and we are sure not to omit anything by such a limitation.

What is the general process of change in a solution while it is being vaporised? The answer is quite distinct: *the residue is always less volatile* than the original solution, and *the distillate more volatile*. If there were an example of a solution behaving in the contrary way, then the process of vaporisation at constant temperature would be an explosive one. For the vapour begins to form at a given pressure; if by this the vapour-pressure of the residue were lowered, the vaporisation would continue of itself at a continually accelerated rate until all the liquid would be vaporised at once. It would be, in other words, a *labile* equilibrium. These equilibria are, however, only mathematical fictions, and have no experimental existence. If, on

the contrary, the residue has a lower vapour-pressure, then the process is self-limiting, and shows the characteristics of a *stable* equilibrium. With hylotropic bodies we have an *indifferent* equilibrium, because the state is independent of the progress of the transmutation.

This being granted, we can ask: if we continue the separation of a solution into a less and a more volatile part by repeated distillation, what will finally become of it? Generally considered, two cases may happen. First the residue may become less and less, and the distillate more and more volatile, and there is no end to the progress. This case we may exclude from experimental evidence of a most general character, for we may take it as a general law that it is impossible to enhance any property beyond all limits, even by the unlimited application of our methods. We must conclude, therefore, that we shall ultimately meet with a *limit of volatility on both sides*, that finally we shall have separated our solution into a least and a most volatile part, and that both parts will not change further by repeated distillation. This is a most interesting result, for it means that *every solution can be resolved into components, which are hylotropic bodies*. For simplicity's sake we have considered only the case that two hylotropic components are generated by the process of separation; generally more than two may be formed, but in every case only a limited number of such components is possible. We may formulate therefore as a general law:

It is possible in every case, to separate solutions into a finite number of hylotropic bodies.

From the components, we can compose the solution again with its former properties. This is also a general experimental law; if exceptions seem to exist, it is only because the case is not one of true equilibrium. Still we may limit our consideration to those cases where the law holds good. Then we have a relation between the properties of any solution, and the nature and relative quantity of its hylotropic components, which admits of only one interpretation. Every solution of distinct properties has also a distinct composition and *vice versa*.

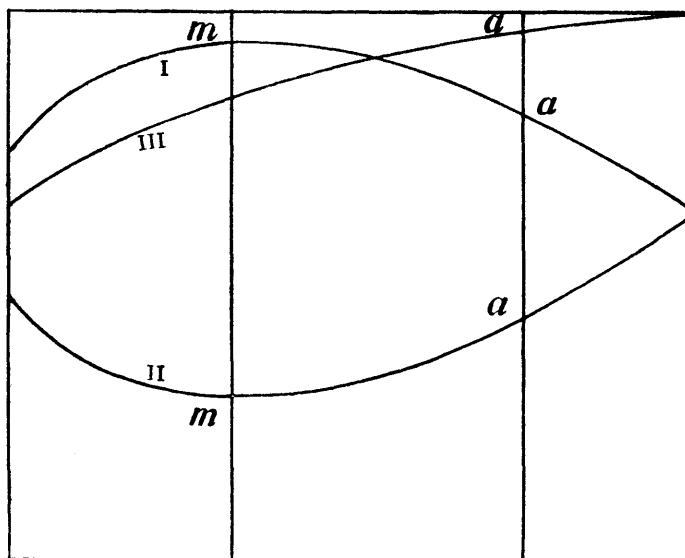
If we consider for simplicity's sake solutions of only *two* components, we may represent any property as depending upon the composition in a rectangular co-ordinate system, the abscissæ giving the composition and the ordinates the value of the property considered. In this way, we get a continuous line of a shape dependent on the particular case chosen.

If we consider the boiling points of all solutions formed by two hylotropic components, the most simple forms of curves (indeed the only experimental ones known) are given by the types I, II, and III, Fig. 3. For any solution, for example, the solution with the abscissa *a*, we can foretell its variation on distillation by the slope of the curve. For as

the residue must be less volatile, the residue will change to the ascending side of the curve. This is for I and III to the right, for II to the left side of the diagram. The change of the *distillate* is the opposite.

If we try to apply this criterion to the points *m* of the curve II and III, where there is a maximum and a minimum of the boiling point, we arrive at no decisive answer, for if the boiling point is already the highest possible it cannot rise, and if it is the lowest possible, it cannot fall. We are forced therefore to conclude that the boiling

FIG. 3.



point cannot change at all, that is, that this special solution must behave as a hylotropic body.

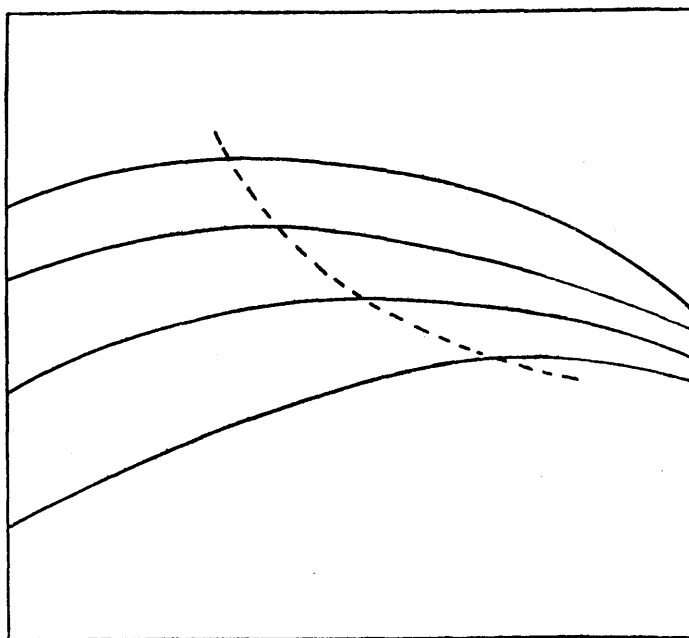
This is a well-known theorem of Gibbs and Konovaloff, to wit, that a maximum or a minimum, generally spoken of as a *distinguishing point* in the boiling-curve, is necessarily connected with the property of distilling without change in the composition of the solution. A similar law holds good for the transitions from liquid to solid and from solid to gas.

Now this looks like a contradiction; while a few minutes ago we placed solutions in a class exclusive of hylotropic bodies, we have here solutions, that is, mixtures, which behave like hylotropic substances. But the contradiction vanishes if we consider a series of boiling-point curves corresponding with various pressures. We then find that the composition at the distinguishing point does not remain constant under different pressures, but shifts to one side, with alteration of pressure. This fundamental fact was discovered and experimentally

developed in an admirable way by Sir Henry Roscoe, and has since proved itself a most important criterion in recognising a chemical individual.

By drawing curves corresponding with various pressures, we get therefore generally the diagram shown in Fig. 4, the loci of the distinguishing points forming one curve. Between the infinite possibilities of the shape of this curve we have a distinguishing case again, the case that the curve is a *vertical straight line*. This means that the composition

FIG. 4.



is independent of the pressure. *When this is the case, we call this hylotropic body a substance or a chemical individual.*

Therefore we conclude that a connection exists between solutions and chemical compounds or substances; the latter being a distinguishing case of the former. On the other hand, we get an exact definition: *a substance or a chemical individual is a body, which can form hylotropic phases within a finite range of temperature and pressure.*

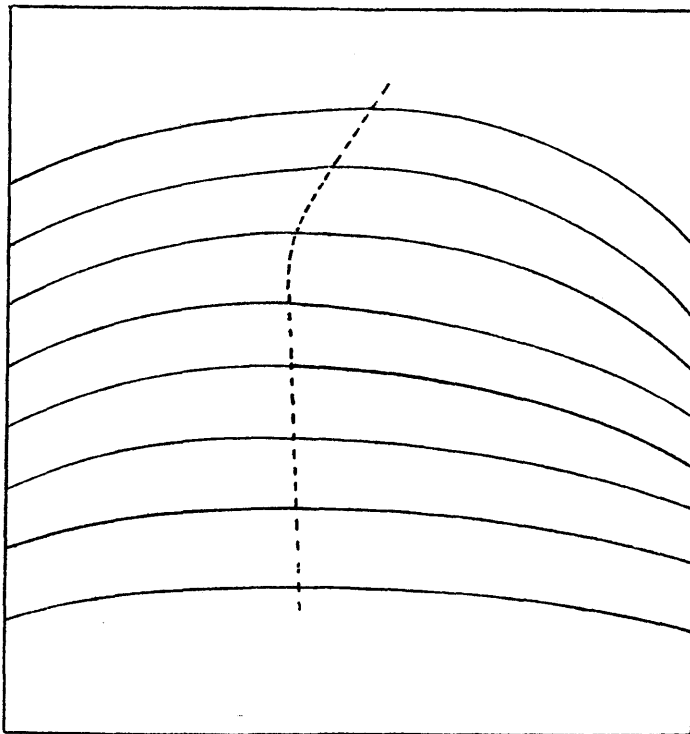
Such substances can often be produced from other substances in the same way as a solution is, namely, by putting them together. If that can be done, we may infer from our definition that there exists a definite ratio between the components, independent of temperature and pressure between certain limits.

Now, *this is essentially the law of definite proportions*, the first of the stoichiometrical laws. We have deduced, therefore, the law of constant proportions from the concept of the chemical individual.

As you have seen, this deduction is extremely simple; the constancy of composition is a natural consequence of the mode of preparation and purification of chemical substances.

If we exceed the limits of temperature and pressure, where the

FIG. 5.



body behaves as a hylotropic one, it assumes the properties of a solution, that is, its distinguishing point begins shifting in composition when the temperature is changed. Then it becomes possible to separate the body into its components, and we call this state the state of dissociation of the substance in question. In our graphic representation, the hitherto straight vertical line of distinguishing points turns sideways, Fig. 5.

Most substances behave in this way, but there are substances which have never been transformed into solutions or whose sphere of existence covers all accessible states of temperature and pressure. Such

substances we call elements. In other words, *elements are substances which never form other than hylotropic phases.*

From this we may conclude that every body is finally transformable into elements, and into only *one definite set of elements*. For the most general case is a solution. Every solution can be separated into a finite number of hylotropic components, and these again can generally be transferred into a state when they behave like solutions and can be separated further. Finally, the components remain hylotropic through the whole range of temperature and pressure, that is, they are elements.

From the fact that the relation between a compound substance and its elements admits of only one qualitative and quantitative interpretation, we derive the conclusion that the resolution of any substance into its elements must always lead to the same elements in the same proportion. Here we find the source of the law of the *conservation of the elements*. This law is not generally expressed as a special stoichiometrical law, because we tacitly infer it from the atomic hypothesis. But it is truly an empirical law, and we see that it is not only a consequence of the atomic hypothesis, but also a consequence of the experimental definition of an element and of our methods of obtaining elements.

Here I should like to pause for a moment for the purpose of quoting a couple of historical facts. Up to the present moment, the question whether it is possible to deduce the stoichiometrical laws without the help of the atomic hypothesis has only been raised by other investigators in order to deny the possibility. So far as I am aware, there exists only one man who has worked upon the question with the earnest hope of obtaining an affirmative answer. Very few know his name. The man is Franz Wald; he is chief chemist at the iron works in Kladno, Bohemia. His papers on the subject are to be found in the *Zeitschrift für physikalische Chemie* and in the *Annalen der Naturphilosophie*.

In the foregoing considerations, Franz Wald has played a great part. To him I owe first the idea that the definition of substances and elements is in a certain sense arbitrary, although very helpful and convenient. This definition is a condensed expression of our methods of separating and purifying these bodies. While, generally speaking, every solution has the same claim to be investigated as these bodies, the latter soon distinguish themselves as standards to which all other cases may be referred. To Franz Wald I owe further the idea that the conception of a *phase* is a far more general one than that of a substance, and that the deduction of the idea of a substance, and, further, the deduction of the laws governing the nature of substances, must start from the conception of the phase. I do not know whether

Wald will agree with the way I have made use of his ideas, but I feel it imperatively necessary to express my deep respect for, and my thankful obligation to, this solitary philosopher, who has prosecuted his work during a long series of years almost wholly without encouragement or sympathy from others.

Now there are still two stoichiometrical laws to be deduced, namely, the law of multiple proportions and the law of combining weights. I prefer to invert the order, and first to deduce the second law. It expresses the fact that it is possible to ascribe to each element a certain relative weight in such a way that every combination between the elements can be expressed by these weights or their multiples.

We suppose three elements, A, B, and C, given, which may form binary combinations, AB, BC, and AC, and besides these a ternary combination, ABC; there shall be but one combination of every kind. Now we begin by forming the combination AB; for this purpose, we must take a certain invariable ratio between the weights of A and B, according to the already proved law of constant proportions. Now we combine AB with C and get the ternary compound, ABC. There will be a certain ratio, too, between AB and C, and we can, if we put A as unity, assign to B and C certain numbers describing their combining weights relatively to A.

Now we begin to combine A with C forming AC, and then we form the ternary combination, ACB from AC and B. According to our law of a relation between elements and compounds, which can be interpreted only in one way, ACB cannot be different from ABC, and, in particular, it must show the same ratio between the relative weights of its elements. Therefore, the ratio of the weights of A and C in forming the combination AC cannot be other than that expressed by the relative combining weights already found in the first way. In other words, it is possible to compute the composition of the hitherto unknown combination AC, from analyses of the combinations AB and ABC. In the same way, we can compute the composition of the unknown combination BC, by the help of the numbers obtained by the analyses of two other combinations of the same elements. To resume: the combining weights relatively to A regulate all other possible compounds between the elements concerned. But this is nothing else than the general stoichiometrical law of combining weights for we can extend our considerations without difficulty to any number of elements.

Lastly, it is easy to deduce the law of multiple proportions from the law of combining weights. If no compounds can be formed except according to their combining weights, then, if there are two different compounds between A and B, we can form the one containing more of B either directly from A and B, or indirectly, combining first A and B

to form the lower compound and then combining this with more of B. In applying the law of combining weights, we conceive that the weight of B in the higher compound must be twice its weight in the lower. The same consideration may be repeated, and finally we get the result, that instead of double the combining weight, *any multiple* of it may occur in combinations, but no other ratio.

If we cast a backward glance on the mental operations we have performed in the last two deductions, we recognise the method, the application of which has made the two laws of energetics so fruitful. In the same manner as the difference between the whole and the available energy is independent of the nature of the path between the same limiting points, the product of the chemical action between a number of given elements is independent of the way in which they are combined. If we compare two different ways, we get an equation between the characteristics of the two ways, and this is equivalent to a new law. In our case, this new law is the law of combining weights.

I will put the same idea into somewhat different words. By stating the equation between any two ways, we can get any number of different equations, each representing a new way as an experimental fact. Now, in order that all these equations shall be consistent, there must be some general law regulating the characteristics of the equations. For the consistency of the several equations in the case under discussion, the existence of specific combining weights, independent of the several combinations, is the necessary condition.

This is the main point of the considerations I wish to lay before you this evening. There are some secondary questions as to isomerides or allotropic states of substances, and there are other similar questions, but it would lead us too far to consider them one by one. I have investigated them on the same basis, and I can assure you that I have nowhere found an insurmountable difficulty or an impassable contradiction. All these facts find their proper place in the frame of the same general ideas.

Let me still add some words about the *nature of the elements*, as considered from my point of view. I wish to lay great stress on the fact that here, too, I find myself on the same ground as that on which Faraday has built his general concepts during his whole scientific career. There is only one difference, due to the development of science. Faraday ever held up the idea that we know matter only by its forces, and that if we take the forces away, there will remain no inert carrier, but really nothing at all. As Faraday still clung to the atomic hypothesis, he was forced to express this idea by the conception that the atoms are only mathematical points whence the forces emerge, or where the directions of the several forces intersect; here his view coincided with that of Boscovich.

In the language of modern science I express these ideas by stating: *what we call matter is only a complex of energies which we find together in the same place.* We are still perfectly free, if we like, to suppose either that the energy fills the space homogeneously, or in a periodic or grained way; the latter assumption would be a substitute for the atomic hypothesis. The decision between these possibilities is a purely experimental question. Evidently there exist a great number of facts—and I count the chemical facts among them—which can be completely described by a homogeneous or non-periodic distribution of energy in space. Whether there exist facts which cannot be described without the periodic assumption, I dare not decide for want of knowledge; only I am bound to say that I know of none.

Taking this general point of view, in what light do we regard the question of the elements? We will find the answer, if we remember that the only difference between elements and compounds consists in the supposed impossibility of proving the so-called elements to be compounds. We are therefore led to ask for the general energetic properties underlying the concept of a chemical individual, whether element or compound.

The answer is most simple. The reason why it is possible to isolate a substance from a solution is that the available energy of the substance is *a minimum*, compared with that of all adjacent bodies. I will not develop this thesis at length, for it is a well-known theorem in energetics or thermodynamics. I will only recall the fact that a minimum of vapour-pressure is always accompanied by a minimum of available energy; and we have already seen that a minimum of vapour-pressure or a maximum of boiling-point is the characteristic of a hylotropic body or chemical individual.

This granted, we proceed to the question regarding the differences between the several substances. Expressed in the most general way, we find these differences connected with differences in their *specific energy-content*. Temperature and pressure are not specific, for we can change them at will. Specific volume and specific entropy, on the contrary, are not changeable at will; every substance has its own values of these. We may take therefore these values as the characteristics of the different substances. How many of such characteristics exist I cannot tell. Only for simplicity's sake I will assume that two of them are sufficient. As I will take care not to deduce any conclusions from this number, we shall not be led into error by accepting it.

We place these two characteristics in a system of planar co-ordinates; then the several elements will be represented by single points in the plane. We lay the plane horizontally and raise from these points ordinates, representing the available energy of each element. Between the points of the elements in the plane are situated the

points of all possible solutions, filling up the whole plane. Each of these solutions will also have its available energy, and all the corresponding points in space will form a continuous surface. The form of this surface can be described in a general way. For as each *element* has its point in a *relative minimum*, the surface as a whole will have a shape like the ceiling of a cavern full of hanging stalactites, the end of each stalactite representing an element.

How can we pass from one element to another? Evidently not otherwise than by going over the higher parts of the surface, or the passes separating each stalactite from its neighbours. This can only be done by accumulating an appropriate amount of available energy in the element to be changed. Now the concentration of energy is a task we cannot accomplish *ad libitum*, for the possibility very soon ends. Think, for example, of compressing a gas into a given space. Up to some ten thousand atmospheres the work of compression will go on smoothly, but after that every metal begins to flow like a liquid and you cannot proceed further. With the concentration of electric or any other energy the task is similar and so we come to the conclusion that the concentration of energy can be pushed to only a very limited extent. The application of this result to our question about elements is simple enough: we cannot get over the pass between two stalactites because we cannot attain the necessary concentration of energy.

From the history of science we learn that these considerations contain at least some truth, for the isolation of the elements has ever been dependent upon the power of concentrating energy available at that time. The most brilliant example is the application of the voltaic pile to the isolation of the alkali metals by Humphry Davy.

Still I must confess that these last considerations are in a very embryonic state, and I should not have brought them before you if an unexpected application had not lately made itself manifest. Some years ago I explained these views to my old friend Sir William Ramsay, when he asked me how the idea of elements fitted into my conceptions of energy. Then I forgot all about it until Sir William reminded me of it, saying that his perplexing discovery of the transmutation of radium into helium might conceivably find some explanation in this way. This I am convinced of, and the considerations may be pictured in the following manner.

In the corner of our cavern where the elements with the highest combining weight are assembled, the stalactites are very short; and at last they are not really stalactites, but rather regions of different slope in the sloping ceiling. In our cavern, a drop of water furnishes generally a picture of the stability of the elements. While hanging at the end of a true stalactite, more or less work must be done

to raise the drop over the pass until it flows down another stalactite. But in this corner it will flow of its own accord, and only delay for a short time on the nearly horizontal portions in the ceiling.

Such elements will have only a *temporary existence*. Now we are sure that for the transmutation of one element into another, enormous amounts of energy would be required, for the concentrations of energy as yet available have proved themselves insufficient for this purpose. We may expect, therefore, that enormous amounts of energy will be liberated if such an unstable element changes into a stable one. This accounts for the extraordinary quantity of energy developed by radium during its existence. The fact that radium changes into helium, an element with an exceptionally long stalactite (for it is impossible to get even any combination of helium) makes us expect indeed such an unusually great development of energy as is found to occur.*

The heat from radium is surely only the last form of the energy developed in its transformation. There are a great many intermediate forms, termed rays or radiations, which have been studied by a band of eminent workers, whose ingenuity and ability have been displayed in the most brilliant way during these investigations. Perhaps I may venture the suggestion that first, other intermediate temporary elements are formed and that the energy liberated at this transmutation appears first in the shape of *new*, still imperfectly known forms. It is most likely that such forms are originated during the decay of the enormously concentrated energy of radium; at the same time it is probable that we have not yet the means of fixing these forms and so preventing their changing into other, more common forms. We should remember that, for example, the conservation of electric energy at a pressure of some thousand volts during some months or years is by no means an easy thing, and I have great doubt if it is possible at all.

But here I must conclude, for I have ventured to intrude on a field where I have not secured my own right of entry by personal work. I see among my audience men who are possessed of an incomparably more minute and comprehensive knowledge of these new realms of science than I. I must ask you, therefore, to take these suggestions in the same spirit as that in which Faraday took his own speculations. They are questions put to nature. If she says Yes, then we may follow the same path a little further. If she says No—well, then we must try another path.

* Compare Soddy, "The Wilde Lecture," *Mem. and Proc. Manchester Lit. and Phil. Soc.*, 1904. I am very glad to find that I am in close agreement (except in so far as there is a difference in his accepting the atomistic, while I hold by the energetic point of view) with this most zealous worker; indeed, the above statements were written and printed before I saw Mr. Soddy's lecture.

BROWNIAN MOVEMENT AND MOLECULAR REALITY.

BY M. JEAN PERRIN

(Professeur de Chimie Physique, Faculté des Sciences,
Université de Paris.)

TRANSLATED FROM THE

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BY F. SODDY, M.A., F.R.S.

I.

1. The first indication of the phenomenon.—When we consider a fluid mass in equilibrium, for example some water in a glass, all the parts of the mass appear completely motionless to us. If we put into it an object of greater density it falls and, if it is spherical, it falls exactly vertically. The fall, it is true, is the slower the smaller the object; but, so long as it is visible, it falls and always ends by reaching the bottom of the vessel. When at the bottom, as is well known, it does not tend again to rise, and this is one way of enunciating Carnot's principle (impossibility of perpetual motion of the second sort).

These familiar ideas, however, only hold good for the scale of size to which our organism is accustomed, and the simple use of the microscope suffices to impress on us new ones which substitute a kinetic for the old static conception of the fluid state.

Indeed it would be difficult to examine for long preparations in a liquid medium without observing that all the particles situated in the liquid instead of assuming a regular movement of fall or ascent, according to their density, are,

a

on the contrary, animated with a perfectly irregular movement. They go and come, stop, start again, *mount*, descend, *remount again*, without in the least tending toward immobility. This is the *Brownian movement*, so named in memory of the naturalist Brown, who described it in 1827 (very shortly after the discovery of the achromatic objective), then proved that the movement was not due to living animalculæ, and recognised that the particles in suspension are agitated the more briskly the smaller they are.

2. Projection of the Brownian movement—This phenomenon can be made visible to a whole audience by projection, but this is difficult, and it may be useful to detail the precautions which have enabled me to arrive at a satisfactory result. The image of an electric arc (or better, of the sun) is formed in the preparation, the greater part of the non-luminous heat rays being stopped by means of a cell full of water. The rays, reflected by the particles in suspension, traverse, as for direct observation, an immersion objective and an eyepiece of high magnification, and are then turned horizontally by a total-reflection prism so as to form the image of the granules on a screen of ground glass (ruled in squares by preference, so as to have reference marks), on the farther side of which the audience is. The light is thus better utilised than with an ordinary screen which would diffuse a large part of it in directions where there were no observers. The magnification can be usefully raised to 8,000 or 10,000 diameters.

But it is necessary above all to procure an appropriate emulsion. In the few trials of projection which have been made up till now, the diameter of the granules employed was of the order of a micron, and their image is visible only with difficulty beyond 3 metres (at least with the light of the arc) whether immersion or lateral illumination is used. Smaller granules are still less visible, and one is led to this, at first sight, paradoxical conclusion, that it is better to project large granules than small ones. It is true that their movement is less, but it is still quite sufficient for its essential characteristics to be easily recognised.

It is still necessary to know how to prepare particles

having a diameter of several microns, and we shall see soon that this is equally desirable in regard to certain points in the experimental study proper of the Brownian movement. I shall indicate later (No. 32) how I have succeeded in obtaining large, perfectly spherical granules of gamboge and mastic. With such granules the Brownian movement can still be perceived at a distance of 8 or 10 metres from the screen in a hall which has been made absolutely dark.

3. Persistence of the phenomenon in absence of all causes external to the fluid. Its explanation by the movements of molecules.—The singular phenomenon discovered by Brown did not attract much attention. It remained, moreover, for a long time ignored by the majority of physicists, and it may be supposed that those who had heard of it thought it analogous to the movement of the dust particles, which can be seen dancing in a ray of sunlight, under the influence of feeble currents of air which set up small differences of pressure or temperature. When we reflect that this apparent explanation was able to satisfy even thoughtful minds, we ought the more to admire the acuteness of those physicists, who have recognised in this, supposed insignificant, phenomenon a fundamental property of matter.

Besides, as happens most frequently when it is sought to unravel the genesis of a great directing idea, it is difficult to fix precisely how the hypothesis, which ascribes the Brownian movement to molecular agitation, first appeared and how it was developed.

The first name which calls for reference in this respect is, perhaps, that of Wiener, who declared at the conclusion of his observations, that the movement could not be due to convection currents, that it was necessary to seek for the cause of it in the liquid itself, and who, finally, almost at the commencement of the development of the kinetic theory of heat, divined that molecular movements were able to give the explanation of the phenomenon*.

Some years later Fathers Delsaulx and Carbonnelle

* *Erklärung des atomistischen Wesens des flüssigen Körperzustandes und Bestätigung desselben durch die sogenannten Molekularbewegungen* (Pogg. Ann. 1863, cxviii. 79).

published in the *Royal Microscopical Society* and in the *Revue des Questions scientifiques*, from 1877 to 1880, various Notes on the *Thermodynamical Origin of the Brownian Movement**. In a note by Father Delsaulx, for example, one may read : "the agitation of small corpuscles in suspension in liquids truly constitutes a general phenomenon," that it is "henceforth natural to ascribe a phenomenon having this universality to some general property of matter," and that "in this train of ideas, the internal movements of translation which constitute the calorific state of gases, vapours and liquids, can very well account for the facts established by experiment."

In another Note, by Father Carbonnelle, one, again, may read this : "In the case of a surface having a certain area, the molecular collisions of the liquid which cause the pressure, would not produce any perturbation of the suspended particles, because these, as a whole, urge the particles equally in all directions. But if the surface is of area less than is necessary to ensure the compensation of irregularities, there is no longer any ground for considering the mean pressure ; the inequal pressures, continually varying from place to place, must be recognised, as the law of large numbers no longer leads to uniformity ; and the resultant will not now be zero but will change continually in intensity and direction. Further, the inequalities will become more and more apparent the smaller the body is supposed to be, and in consequence the oscillations will at the same time become more and more brisk"

These remarkable reflections unfortunately remained as little known as those of Wiener. Besides it does not appear that they were accompanied by an experimental trial sufficient to dispel the superficial explanation indicated a moment ago ; in consequence, the proposed theory did not impress itself on those who had become acquainted with it.

On the contrary, it was established by the work of M. Gouy (1888), not only that the hypothesis of molecular agitation gave an admissible explanation of the Brownian movement, but that no other cause of the movement could

* See for this bibliography an article which appeared in the *Revue des Questions scientifiques*, January 1909, where M. Thirion very properly calls attention to the ideas of these *savants*, with whom he collaborated.

be imagined, which especially increased the significance of the hypothesis*. This work immediately evoked a considerable response, and it is only from this time that the Brownian movement took a place among the important problems of general physics.

In the first place, M. Gouy observed that the Brownian movement is not due to vibrations transmitted to the liquid under examination, since it persists equally, for example, at night on a sub-soil in the country as during the day near a populous street where heavy vehicles pass. Neither is it due to the convection currents existing in fluids where thermal equilibrium has not been attained, for it does not appreciably change when plenty of time is given for equilibrium to be reached. Any comparison between Brownian movement and the agitation of dust-particles dancing in the sunlight must therefore be set aside. In addition, in the latter case, it is easy to see that the neighbouring dust-particles move in general in the same sense, roughly tracing out the form of the common current which bears them along, whereas the most striking feature of the Brownian movement is the absolute independence of the displacements of neighbouring particles, so near together that they pass by one another. Lastly, neither can the unavoidable illumination of the preparation be suspected, for M. Gouy was able abruptly to reduce it a thousand times, or to change its colour considerably, without at all modifying the phenomenon observed. All the other causes from time to time imagined have as little influence; even the nature of the particles does not appear to be of any importance, and henceforward it was difficult not to believe that these particles simply serve to reveal an internal agitation of the fluid, the better the smaller they are, much as a cork follows better than a large ship the movements of the waves of the sea.

Thus comes into evidence, in what is termed a *fluid in equilibrium*, a property eternal and profound. This equilibrium only exists as an average and for large masses; it is a statistical equilibrium. In reality the whole fluid is

* *Journal de Physique*, 1888, 2nd Series, vii. 561; *Comptes rendus*, 1889, cix. 102; *Revue générale des Sciences*, 1895, 1.

agitated indefinitely and *spontaneously* by motions the more violent and rapid the smaller the portion taken into account; the statical notion of equilibrium is completely illusory.

4. Brownian movement and Carnot's principle.—There is therefore an agitation maintained indefinitely without external cause. It is clear that this agitation is not contradictory to the principle of the conservation of energy. It is sufficient that every increase in the speed of a granule is accompanied by a cooling of the liquid in its immediate neighbourhood, and likewise every decrease of speed by a local heating, without loss or gain of energy. We perceive that thermal equilibrium itself is also simply a statistical equilibrium. But it should be noticed, and this very important idea is again due to M. Gouy, that the Brownian movement is not reconcilable with the rigid enunciations too frequently given to Carnot's principle; the particular enunciation chosen can be shown to be of no importance. For example, in water in equilibrium it is sufficient to follow with the eyes a particle denser than water to see it at certain moments rise spontaneously, absorbing, necessarily, work at the expense of the heat of the surrounding medium. So it must not any longer be said that perpetual motion of the second sort is impossible, but one must say: "On the scale of size which interests us practically, perpetual motion of the second sort is in general so insignificant that it would be absurd to take it into account." Besides such restrictions have long been laid down: the point of view that Carnot's principle expresses simply a law approximated to has been upheld by Clausius, Maxwell, Helmholtz, Boltzmann, and Gibbs, and in particular may be recalled the *demon*, imagined by Maxwell, which, being sufficiently quick to discern the molecules individually, made heat pass at will from a cold to a hot region without work. But since one is limited to the intervention of invisible molecules, it remained possible, by denying their existence, to believe in the perfect rigidity of Carnot's principle. But this would no longer be admissible, for this rigidity is now in opposition to a *palpable reality*.

On the other hand, the practical importance of Carnot's principle is not attacked, and I hardly need state at length

that it would be imprudent to count upon the Brownian movement to lift the stones intended for the building of a house. But the comprehension of this important principle becomes in consequence more profound : its connection with the structure of matter is better understood, and the conception is gained that it can be enunciated by saying that spontaneous co-ordination of molecular movements becomes the more improbable the greater the number of molecules and the greater the duration of time under consideration*.

5. The kinetic molecular hypothesis.—I have said that the Brownian movement is explained, in the theory of M. Gouy and his predecessors, by the incessant movements of the molecules of the fluid, which striking unceasingly the observed particles, drive about these particles irregularly through the fluid, except in the case where these impacts exactly counterbalance one another. It has, to be sure, been long recognised, especially in explanation of the facts of diffusion, and of the transformation of motion into heat, not only that substances in spite of their homogeneous appearance, have a discontinuous structure and are composed of separate *molecules*, but also that these molecules are in incessant agitation, which increases with the temperature and only ceases at absolute zero.

Instead of taking this hypothesis ready made and seeing how it renders account of the Brownian movement, it appears preferable to me to show that, possibly, it is logically suggested by this phenomenon alone, and this is what I propose to try.

What is really strange and *new* in the Brownian movement is, precisely, that it never stops. At first that seems in contradiction to our every-day experience of friction. If for example, we pour a bucket of water into a tub, it seems natural that, after a short time, the motion possessed by the liquid mass disappears. Let us analyse further how this apparent equilibrium is arrived at : all the particles had at

* With regard to the general significance of the principle I should refer to the very interesting considerations developed by J. H. Rosny, Senior, in his book on Pluralism, pp. 85-91 (F. Alcan, 1909).

first velocities almost equal and parallel ; this co-ordination is disturbed as soon as certain of the particles, striking the walls of the tub, recoil in different directions with changed speeds, to be soon deviated anew by their impacts with other portions of the liquid. So that, some instants after the fall, all parts of the water will be still in motion, but it is now necessary to consider quite a small portion of it, in order that the speeds of its different points may have about the same direction and value. It is easy to see this by mixing coloured powders into a liquid, which will take on more and more irregular relative motions.

What we observe, in consequence, so long as we can distinguish anything, is not a cessation of the movements, but that they become more and more chaotic, that they distribute themselves in a fashion the more irregular the smaller the parts.

Does this de-co-ordination proceed indefinitely ?

To have information on this point and to follow this de-co-ordination as far as possible after having ceased to observe it with the naked eye, a microscope will be of assistance, and microscopic powders will be taken as indicators of the movement. Now these are precisely the conditions under which the Brownian movement is perceived : we are therefore *assured* that the de-co-ordination of motion, so evident on the ordinary scale of our observations, does not proceed indefinitely, and, on the scale of microscopic observation, we *establish* an equilibrium between the co-ordination and the de-co-ordination. If, that is to say, at each instant, certain of the indicating granules stop, there are some in other regions at the same instant, the movement of which is re-co-ordinated automatically by their being given the speed of the granules which have come to rest. So that it does not seem possible to escape the following conclusion :

Since the distribution of motion in a fluid does not progress indefinitely, and is limited by a spontaneous re-co-ordination, it follows that the fluids are themselves composed of granules or *molecules*, which can assume all possible motions relative to one another, but in the interior of which dissemination of motion is impossible. If such molecules

had no existence it is not apparent how there would be any limit to the de-co-ordination of motion.

On the contrary if they exist, there would be, unceasingly, partial re-co-ordination ; by the passage of one near another, influencing it (it may be by *impact* or in any other manner), the speeds of these molecules will be continuously modified, in magnitude and direction, and from these same chances it will come about sometimes that neighbouring molecules will have concordant motions. In addition, even without this absolute concordance being necessary, it will at least come about frequently that the molecules in the region of an indicating particle will assume in a certain direction an excess of motion sufficient to drive the particle in that direction.

The Brownian movement is permanent at constant temperature : that is an experimental fact. The motion of the molecules which it leads us to imagine is thus itself also permanent. If these molecules come into collision like billiard balls, it is necessary to add that they are perfectly elastic, and this expression can, indeed, be used to indicate that in the molecular collisions of a thermally isolated system the sum of the energies of motion remains definitely constant.

In brief the examination of Brownian movement alone suffices to suggest that every fluid is formed of elastic molecules, animated by a perpetual motion.

6. The atoms. Avogadro's constant.—From this, as is well known, diverse considerations of chemistry, and particularly the study of substitution, lead to the idea of the existence of atoms. When, for example, calcium is dissolved in water, only one half of the hydrogen contained in the latter is displaced. The hydrogen of this water, and in consequence the hydrogen of each molecule, is therefore composed of two distinct parts. No experiments lead to any further differentiation, and it is reasonable to regard these two parts as indivisible, by all chemical methods, or in a word, they are *atoms*. On the other hand, every mass of water, and in consequence each molecule of water, weighs 9 times the hydrogen it contains : the molecule of water, which contains

2 atoms of hydrogen, weighs therefore 18 times the atom of hydrogen. In a similar manner, it may be established that the molecule of methane, for example, weighs 16 times more than the atom of hydrogen. Thus, by a purely chemical method, through the conception of the atom, the ratio 16/18, of the weight of a molecule of methane to a molecule of water, can be reached.

Now this same ratio, precisely, is arrived at by comparison of the masses of similar volumes of methane and water vapour in the gaseous state under similar conditions of temperature and pressure. Thus these two masses, which have the same ratio as the two kinds of molecules, must contain as many molecules the one as the other. This result is general for the different gases, so that in consequence we arrive, in an experimental manner, at the celebrated proposition enunciated in the form of an hypothesis by Avogadro, about a century ago, and taken up again a little later by Ampère:

“Any two gases, taken under the same conditions of temperature and pressure, contain in the same volume the same number of molecules.”

It has become customary to name as the gram-molecule of a substance, the mass of the substance which in the gaseous state occupies the same volume as 2 grams of hydrogen measured at the same temperature and pressure. Avogadro's proposition is then equivalent to the following:

“Any two gram-molecules contain the same number of molecules.”

This invariable number N is a universal constant, which may appropriately be designated *Avogadro's Constant*. If this constant be known, the mass of any molecule is known: even the mass of any atom will be known, since we can learn by the different methods which lead to chemical formulæ, how many atoms of each sort there are in each molecule. The weight of a molecule of water, for example, is $\frac{18}{N}$; that of a molecule of oxygen is $\frac{32}{N}$, and so on for each molecule. Similarly the weight of the oxygen atom,

obtained by dividing the gram-atom of oxygen by N , is $\frac{16}{N}$; that of the atom of hydrogen is $\frac{1.008}{N}$, and so on for each atom.

7. The constant of molecular energy.—It is easy to see that if we know Avogadro's constant we can calculate the mean kinetic energy of translation of different molecules, and conversely, the value of this energy will give us N . Let us elaborate this important point a little.

If fluids are composed of molecules in motion, the pressure which they exert on the boundaries which limit their expansion is accounted for by the impacts of their molecules against these boundaries, and, in the case of gases (the molecules of which are very remote, relatively, one from another), it has been established, thanks to the successive arguments, created or modified by Joule, Clausius, and Maxwell, that this conception, at first somewhat vague, contains the precise relation

$$pv = \frac{2}{3}nw$$

where p is the pressure which n molecules of mean kinetic energy w develop in the volume v .

If the mass of gas under consideration is one gram-molecule, n becomes equal to N and pv to RT , T being the absolute temperature and R the constant of a perfect gas (equal in c.g.s. units to 83.2×10^6); the preceding equation may then be written

$$\frac{2}{3}Nw = RT$$

or

$$w = \frac{3R}{2N}T.$$

Now the constant N is the same for all substances. The molecular kinetic energy of translation has thus for all gases the same mean value, proportional to the absolute temperature

$$w = \alpha T.$$

The constant α , which may be named the *constant of molecular energy*, equal to $\frac{3R}{2N}$, is, like N , a universal constant.

It is evident that both of these constants will be known as soon as one is.

8. The atom of electricity.—A third universal constant is also reached at the same time as N or α , and this is encountered in the study of the phenomena of electrolysis. It is known that the *decomposition* by the current of the gram-molecule of a given electrolyte is accompanied always by the passage of the same quantity of electricity: as is well known, this is explained by the conception that in all electrolytes a part at least of the molecules are dissociated into *ions* carrying fixed electric charges, and in consequence sensitive to the electric field; lastly, if the name *faraday* is given to the quantity F of electricity (96,550 coulombs) which passes in the decomposition of 1 gram-molecule of hydrochloric acid, it is known that the decomposition of any other gram-molecule is accompanied by the passage of a whole number of faradays, and, in consequence, that any ion carries a whole number of times the charge on the hydrogen ion. This charge e thus also appears as indivisible, and constitutes the atom of electricity or the electron (Helmholtz).

It is easy to obtain this universal constant if either of the constants, N or α , is known. Since the gram-atom of hydrogen in the ionic state, that is to say N atoms of hydrogen, carries one faraday, then necessarily,

$$Ne = F,$$

which is, in c.g.s. electrostatic units,

$$Ne = 96,550 \times 3.10^9 = 29.10^{13};$$

thus, in the same step, the three universal constants N , e , α will be found. Can this be accomplished?

9. Molecular speeds. Maxwell's law of irregularities. Mean free path.—The commencement of the answer to this question, and, at the same time, the approximate determination of the

order of molecular magnitude, is due to the admirable efforts of Clausius, Maxwell, and Van der Waals. Without entering into detail I think it useful to summarise the line they have followed.

First, for each gas the mean square, U^2 , of the molecular speed is easily calculated from the equation just written

$$\frac{2}{3}Nw = RT.$$

It is sufficient to notice that $2Nw$ can be replaced by MU^2 , M representing the gram-molecule of the gas under consideration. Thus it is found that U is of the order of some hundreds of metres per second (435 metres at 0° for oxygen).

As well understood, the molecular speeds are very variable and unequal; but in a steady state the proportion of molecules which have any definite speed remains fixed. On the hypothesis that the probability of a component x is independent of the values of the components y and z , Maxwell succeeded in determining the law of distribution of molecular speeds. His reasoning demonstrated that, on this hypothesis, the probability of any molecule possessing, along the axis Ox , a component between x and $x + dx$ had the value

$$\frac{1}{U} \sqrt{\frac{3}{2\pi}} e^{-\frac{3}{2} \frac{x^2}{U^2}} dx.$$

This expression represents the irregularities of molecular motion. It is obtained just the same on the hypothesis that the components along the Ox axis are distributed around the zero value according to the so-called law of *chance* enunciated by Laplace and Gauss.

This *law of the distribution of velocities* permits the calculation of the mean speed Ω , which is not equal to U (any more than $\frac{a+b}{2}$ is equal to the square root of $\frac{a^2+b^2}{2}$), but which, as a matter of fact, differs but little from it

$$\left(\Omega = U \sqrt{\frac{8}{3\pi}} \right).$$

On the other hand, this same law of distribution can be used

to test by calculation the hypothesis that the *internal friction* between two parallel layers of gas, moving at different speeds, results from the continuous arrival, in each layer, of molecules coming from the other layer. Maxwell in this way found that the coefficient ζ of internal friction, or viscosity, which is experimentally measurable, should be very nearly equal to one-third of the product of the following three quantities: the absolute density δ of the gas (given by the balance), the mean molecular speed Ω (which we know how to calculate), and the mean free path L which a molecule traverses in a straight line between two successive impacts. More exactly, he found

$$\zeta = 0.31 \delta \Omega L.$$

The value of the mean free path is thus obtained: for example, for oxygen or nitrogen at ordinary temperature and under atmospheric pressure it is approximately equal to 0.1 micron. At the low pressure of a Crookes' tube it can reach many centimetres.

10. The relation of the mean free path of the molecule to its diameter.—In addition, a line of reasoning, due to Clausius, shows that this same mean free path can be calculated in another manner as a function of the nearness of approach of the molecules and of their dimensions*. It is easy to understand that the smaller the molecules are the nearer their approach, and the larger they are the more they act as obstructions.

But there are certainly other considerations to be taken into account, as, for example, that a molecule in the form of a rod (as in the case, possibly, of certain molecules of the fatty series) will not obstruct in the same way as if it had the form of a sphere. In default of any knowledge of the exact shape of molecules, it has been thought that no great error is likely to result in likening them to spherical balls, having a diameter equal to the mean distance apart of the centres of two molecules on impact. This hypothesis, possibly exact in the case of monatomic molecules (mercury, argon, etc.), is certainly false for other molecules, but it is

* *Pogg. Ann.* 1858.

still possible that it may lead to approximate results in the case of the less complicated molecules such as those of oxygen and nitrogen.

Let us then liken the molecules to spheres. The approximate calculation of Clausius, subsequently modified by Maxwell, showed that the following relation should hold approximately,

$$L = \frac{1}{\pi\sqrt{2}} \frac{1}{nD^2},$$

where D represents the molecular diameter, and n the number of molecules contained in each cubic centimetre. Since L can be calculated, a second relation between n and D will give us the diameter of the molecules and the number n per cubic centimetre. In this case, multiplying the number n by the known volume of the gram-molecule under the conditions of temperature and pressure chosen in the calculation, we shall have the number N of molecules in a gram-molecule, *that is to say the required three universal constants.*

But this second relation between n and D has not been very easy to obtain.

11. First determinations of Avogadro's constant.—To begin with, the molecules in the liquid state cannot be more closely packed than bullets are in a pile of bullets*. Now it is easily established that the volume of bullets is only equal to 73 per cent. of the volume of the pile. So, we have

$$\frac{1}{6} \pi n D^3 < 0.73 \phi,$$

where ϕ signifies the known volume occupied by the mass of a cubic centimetre of the gas considered in the liquid state at low temperature. This inequality combined with the preceding equation, which gives the product nD^2 , leads to a value certainly too great for the molecular diameter, and therefore to values certainly too small for n and N .

The calculation is usually made for oxygen (which gives

* In reality, the original reasoning, due to Loschmidt, was limited to the statement that the volume of the molecules is inferior to that of the liquid and perhaps not more than ten times smaller.

$N > 9.10^{22}$): it is better to make it for a monatomic gas, for which the molecules may really be spherical, and recommencing the calculation for mercury, the mean free path of which at 370° is 21.10^{-6} (Landolt's Tables), I find for the inferior limit of N a higher and therefore more useful value, namely

$$N > 45.10^{22}.$$

As for the molecular diameter, for all the gases considered it is found to be less than the millionth of a millimetre (for the special case of mercury $D < 3.5 \times 10^{-8}$).

This indication only puts us in the same position as that of an astronomer who, desiring to know the distance of a star from the Sun, finds at first only that it is farther off from it than Neptune. Failing a precise measurement, at least it is desirable to close in this star between two limits and to know for example whether it is nearer than Sirius.

This second limit can be fixed from a theory of dielectrics due to Clausius and Mossotti: on this theory the dielectric power of a gas depends upon the polarisation of each molecule by influence by the displacement of interior electric charges. Developing this hypothesis, we shall write that the true volume of n molecules is not equal (as is sometimes stated) but certainly greater than the volume u of n perfectly conducting spheres which could be put in the place of the molecules without modifying the dielectric constant K of the medium. An electrostatic calculation gives to u the value $\frac{K-1}{K+2}$; one can thus write

$$\frac{1}{6} \pi n D^3 > \frac{K-1}{K+2}.$$

The constant K , being practically equal to the square of the refractive index (Maxwell), can also be measured directly.

Applying to the case of argon and obtaining nD^2 from Clausius's equation, we obtain

$$N < 200.10^{22}.$$

As for the molecular diameter, it is found, for all the gases so considered, to be greater than a ten-millionth of a millimetre (for the special case of argon $D > 1.6 \times 10^{-8}$).

Here are, therefore, the various molecular magnitudes confined between two limits, which as regards the weight of each molecule are to one another as 45 is to 200. That we have no better estimate is mainly because we only know how to evaluate roughly the true volume of n molecules which occupy the unit volume of gas. A more delicate analysis is due to Van der Waals, who appears to have obtained as much in connection with molecular magnitudes as the calculation from the mean free path is able to yield *. The gas equation was obtained by supposing the molecules sufficiently separated from one another for their true volume to be small compared with that occupied by their trajectories and that each molecule suffers no sensible influence, similar to cohesion, attracting it towards the whole of the others. Van der Waals was successful in allowing for these two neglected complications and obtained the celebrated equation

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT,$$

approximately true for the whole fluid state, in which the particular nature of the substance studied comes into evidence through the two constants a and b , of which a represents the influence of cohesion, and b exactly four times the true volume of the molecules of the given mass. Hence once b is known, the equation

$$\frac{1}{6}\pi n D^3 = \frac{b}{4}$$

in conjunction with the equation of Clausius and Maxwell

$$\pi n D^2 = \frac{1}{L\sqrt{2}},$$

enables the unknown n and D to be calculated.

This calculation has been made for oxygen and nitrogen and a value for N nearly equal to 45.10^{22} has been obtained: this choice of substances is not a very suitable one, since it necessitates the consideration of the *molecular diameter* for molecules assuredly not spherical. By utilising for the

* *Continuité des états liquides et gazeux*, 1873.

calculation the values recently given for argon, near its critical point, I find

$$N = 62.10^{22}.$$

I should add that it is not easy to estimate the error possibly affecting this number, because of the lack of rigour of the equation of Clausius-Maxwell and of that of Van der Waals. Unquestionably an uncertainty of 30 per cent. will not be a matter for surprise.

With the determination of Van der Waals we reach the end of the first series of efforts. By methods completely different we proceed to consider similar results for which the determination can be made with greater accuracy.

12. The equipartition of energy.—We have seen that the mean molecular energy is, at the same temperature, the same for all gases. This result remains valid when the gases are mixed. It is indeed known that each gas presses upon the enclosure *as if it alone were present*, that is to say that n molecules of this gas develop in the volume v the same partial pressure as if they were alone, in such a way that $\frac{3}{2} \frac{pv}{n}$ preserves the same value. On the other hand, when we try to repeat the reasoning which led to the relation

$$pv = \frac{2}{3} nw,$$

it is found that this reasoning remains applicable. Thus w must preserve the same value. For example, the molecules of carbon dioxide and water vapour, present in the air, must have the same mean kinetic energy in spite of the difference of their natures and their masses.

This invariability of molecular energy is not confined to the gaseous state, and the beautiful work of Van't Hoff has established that it extends to the molecules of all dilute solutions. Let us imagine that a dilute solution is contained in a *semi-permeable* enclosure, which separates it from the pure solvent: we suppose this enclosure allows free passage to the molecules of the solvent, in consequence of which these molecules cannot develop any pressure, but that it

stops the dissolved molecules. The impacts of these molecules against the enclosure will then develop an *osmotic pressure* P , and it is seen, if the reasoning is considered in detail, that the pressure produced by these impacts can be calculated as in the case of a gas, so that in consequence we write

$$Pv = \frac{2}{3} nW,$$

W signifying the mean kinetic energy of translation of n molecules contained in the volume v of the enclosure.

Now Van't Hoff has observed that the experiments of Pfeffer give for the osmotic pressure a value equal to the pressure which would be exerted by the same mass of dissolved substance if it alone occupied in the gaseous state the volume of the enclosure. W is thus equal to w : the molecules of a dissolved substance have the same mean energy as in the gaseous state.

I wish to make a remark on this matter which appears to me to render intuitive an important proposition which the kinetic theory of fluids establishes in a somewhat laborious manner. Van't Hoff's law tells us that a molecule of ethyl alcohol in solution in water has the same energy as one of the molecules of vapour over the solution; it would still have this energy if it were present in chloroform (that is to say if it were surrounded by chloroform molecules), or even if it were in methyl or propyl alcohol: this indifference to the nature of the molecules of the liquid in which it moves makes it almost impossible to believe that it would not still have the same energy if it were in ethyl alcohol; that is if it forms one of the molecules of pure ethyl alcohol. It therefore follows that the molecular energy is the same in a liquid as in a gas, and we can now say:

At the same temperature all the molecules of all fluids have the same mean kinetic energy, which is proportional to the absolute temperature.

But this proposition, already so general, can be still further enlarged. According to what we have just seen,

b 2

the heavy molecules of sugar which move in a sugar solution have the same mean energy as the agile molecules of water. These sugar molecules contain 35 atoms; the molecules of sulphate of quinine contain more than 100 atoms, and the most complicated and heaviest molecules to which the laws of Van't Hoff (or of Raoult which are deduced from them) can be extended may be cited. The mass of the molecule appears absolutely unlimited.

Let us now consider a particle a little larger still, itself formed of several molecules, in a word a *dust*. Will it proceed to react towards the impact of the molecules encompassing it according to a new law? Will it not comport itself simply as a very large molecule, in the sense that its mean energy has still the same value as that of an isolated molecule? This cannot be averred without hesitation, but the hypothesis at least is sufficiently plausible to make it worth while to discuss its consequences.

Here we are then taken back again to the observation of the particles of an emulsion and to the study of this wonderful movement which most directly suggests the molecular hypothesis. But at the same time we are led to render the theory precise by saying, not only that each particle owes its movement to the impacts of the molecules of the liquid, but further that the energy maintained by the impacts is on the average equal to that of any one of these molecules.

The propositions, of which I have just shown the probability, could be looked upon as special cases of the famous theorem of the *equipartition of energy* which, with Maxwell's *law of distribution of velocities*, forms the central point of the mathematical theory of molecular motion. This theorem, solved in successive steps, thanks to very numerous attempts, among which may be cited those of Maxwell, Gibbs, Boltzmann, Jeans, Langevin and Einstein, leads to the statement of the mean equality, as regards each *degree of freedom*, of the kinetic energies of translation or of rotation which are assumed in the interior of a fluid consisting of any assemblage of molecules. This theorem has had great importance even beyond the matters here broached, and, for example, it has been the means of predicting, according to

the number of atoms in a molecule of gas, the ratio between the specific heats of a gas (at constant pressure and constant volume respectively). But its *proof* calls for complicated calculations, and a more simple, even if less rigorous method, has appeared to me desirable. Besides the word *theorem* should not cause illusion, for hypotheses are introduced or implied in the calculations, as in almost all theories of mathematical physics.

I need hardly say that this is not a criticism, and I think, on the contrary, that the great strength of mathematical physics, in its useful application to research and invention, consists in the bringing to light, according to correct logic (conscious or intuitive) of probabilities which qualitative reasoning would not have disclosed. As is well understood, it cannot be maintained that the theories are sufficient to establish the results they indicate without submitting them to the test of experiment.

In brief, whatever the path pursued, we are led to regard the mean energy of translation of a molecule as equal to that possessed by the granules of an emulsion. So that if we find a means of calculating this granular energy in terms of measurable magnitudes, we shall have at the same time a means of proving our theory. The experiments once made, two cases in general can present themselves. Either the numbers found will be greatly different from those given by the kinetic reasoning referred to above, and in this case, above all, if these numbers change according to the granules studied, the credit of the kinetic theories will be weakened and the origin of the Brownian movement remains undiscovered; or, the numbers will be of the order of magnitude predicted, and, in this case, not only shall we have the right to regard the molecular theory of this movement as established, but further we can seek from our experiments, a means, possibly this time exact, of determining molecular magnitudes. I hope to show that experiment has pronounced decisively in this latter direction*.

* My results were published in the *Comptes rendus* of May 1908 and September 1909.

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Dalton suggested that elements were composed of simple atoms; this hypothesis enabled him to explain the laws of chemical combination, but his critics were able to urge that such an explanation was not worth having, that it was purely speculative, and that it involved far too many fundamental particles.

In the end, it was the development of the kinetic theory of gases, and the need to explain isomerism and the Brownian Motion, which made belief in atoms general just at the moment when the researches of J. J. Thomson, of the Curies, and of Rutherford, were establishing that atoms were complex bodies which could be split.

THE EDITOR. David Knight was born in 1936; he took a degree in chemistry at Oxford and remained there to take the Diploma in History and Philosophy of Science. He then wrote a doctoral thesis concerned with nineteenth-century speculations about the chemical elements. In 1964 he was appointed to the first lectureship in History of Science at Durham University and since 1966 he has been a member of the Council of the British Society for the History of Science. He has written various articles on nineteenth-century chemistry and, in 1967, published a book entitled *Atoms and Elements*. He is married, with three small children.

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